Rigid Five- and Six-Membered C,N,N′-Bound Aryl, Benzyl, and Alkyl Organopalladium Complexes: sp^2 vs sp^3 C–H Activation during Cyclopalladation and Palladium(IV) Intermediates in Oxidative Addition Reactions with Dihalogens and Alkyl Halides

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Received October 2, 1992

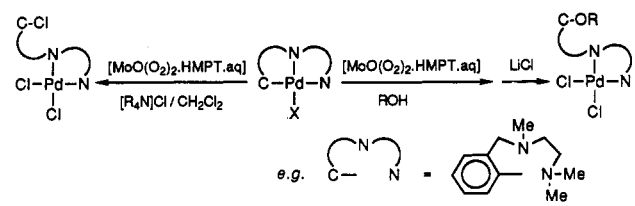
The synthesis of new terdentate C,N,N′-bound aryl, benzyl, and alkyl organopalladium compounds (N,N′ is $-CH_2N(Me)CH_2CH_2NMe_2$ or $-CH_2N(CH_2CH_2)_2NMe$) via cyclopalladation is reported. X-ray crystal structure determinations of [PdI{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (**2c**) and [PdI{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (**3c**) have been carried out. By suitable ligand design, the palladation can be directed toward sp^2 or sp^3 C–H activation and toward five-membered or six-membered ring formation. A study of coordination adducts of the bidentate N_2 part of the terdentate C,N,N′ ligands with PdX_2 has revealed that the C–H bond activation likely proceeds via loss of an acido anion (X) to an electron-deficient, cationic 14-electron species [C,N,N′PdX] that subsequently attacks an intramolecular C–H bond via an in-plane interaction. The crystal structure of the PdI_2 coordination adduct of *N*-(2-iodobenzyl)-*N*,*N*′,*N*′-trimethylethane-1,2-diamine (**7e**) shows an oblique, above-plane approach of the aryl ring toward the metal center with the C–H bond in the ortho position with respect to the ethylenediamine unit pointing toward an iodine atom, the hydrogen atom being involved in short nonbonding contacts with both this iodine atom (3.02(2) Å) and the palladium center (2.97(2) Å). Crystals of **2c** are orthorhombic, space group *Pnaa*, a = 8.5216(3) Å, b = 17.6034(5) Å, c = 18.8696(8) Å, Z = 8, R = 0.038 for 2677 observed reflections with $I > 2.5\sigma(I)$ and 157 parameters. Crystals of **3c** are monoclinic, space group $P2_1/c$, a = 9.506(1) Å, b = 13.582(1) Å, c = 13.148(1) Å, β = 91.36(4)°, Z = 4, R = 0.021 for 3326 observed reflections with $I > 2.5\sigma(I)$ and 249 parameters. Crystals of **7e** are triclinic, space group $P\bar{1}$, a = 8.545(1) Å, b = 8.797(1) Å, c = 13.829(1) Å, α = 81.77(1)°, β = 75.47(1)°, γ = 63.33(1)°, Z = 2, R = 0.064 for 2810 observed reflections with $I > 2.5\sigma(I)$ and 175 parameters. A conformational analysis of **7e** by means of ^1H NMR spectroscopy showed that the solid-state structure is likely retained to a large extent in solution. Based on sp^2/sp^3 C–H activation competition in two ligands, it is concluded that this approach may be responsible for the generally easier palladation of aryl rings compared to alkyl groups. The use of these rigid C,N,N′-bound palladium complexes in controlling their behavior in oxidative addition/reductive elimination reactions is exemplified by the detection of an unusually stable organometallic Pd(IV) dichloride adduct and by the use of a C,N,N′ group as spectator ligand in oxidative addition/reductive elimination reactions with alkyl halides.

Introduction

During our work on the reactivity of organopalladium compounds toward inorganic peroxo species[1] we have prepared several terdentate, C,N,N′-bound, organopalladium complexes, which were convenient substrates for the study of these reactions (Scheme I).[1b]

We found that these and other related terdentate palladium complexes are readily obtained by direct cyclopalladation of the bidentate N,N-bound ligands. The ligands used are both N,N-substituted ethylenediamines and piperazines. Such N,N-bidentate chelating ligands impose a much higher degree of stereochemical control on the coordination sphere around the metal than analogous monodentate systems. This control could provide a means to understand which structural constraints of the ligand as well as of the binding locus around the metal are required in order for cyclometalation to occur. In this study we have begun to explore not only how the ligands that are modeled by variation of the substituents attached to the N,N-chelating bridge or by variation of the chelating unit itself (NCH_2CH_2N or $N(CH_2CH_2)_2N$) can be employed to give preferentially aromatic or aliphatic C–H activation

Scheme I



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0276-7333/93/2312-1831$04.00/0

but also how this modeling steers the C–H activation selectively in the direction of formation of either five- or six-membered rings.

The mechanistic aspects of cyclopalladation have been the subject of recent extensive reviews by Ryabov and Dunina.[2] It is generally accepted that cyclopalladation is initiated by coordination of a heteroatom to the metal, which is followed by ligand dissociation from the square planar 16-electron complex to give a highly reactive, three-coordinate, 14-electron species. This intermediate subsequently activates a C–H bond in a kinetically controlled electrophilic step with a marked preference for the formation of a five-membered chelate ring and attack on an aromatic ring. However, apart from the initial coordination of the hetero atom, all the above-mentioned features are subject to exceptions, and this mechanistic picture of cyclopalladation provides, at best, some guidelines and not pertinent rules. Thus, it has been argued that azobenzene[3] and tri-*tert*-butylphosphine[4] are probably cyclopalladated through a 16-electron pathway, and it is now recognized that palladium(II) exhibits pseudo-nucleophilic instead of electrophilic properties in acetic acid.[5] Furthermore, the benzylideneamine 2,4,6-$(CH_3)_3C_6H_2CH{=}NCH_2C_6H_5$ is metalated exclusively at a mesityl methyl group with six-membered ring formation, even though aromatic metalation at the phenyl ring would lead to a five-membered chelate ring.[6] The preference of methyl C–H activation over activation of an aromatic C–H bond is remarkable since a benzylic M–CH_2Ar bond is weaker than an aromatic M–Ar bond; it has been argued that the position of hydrocarbon activation equilibria is determined by the product's M–C bond strength and not by the reactant's C–H bond strength.[7] The occurrence of such exceptions warrants further investigation of the mechanism of cyclopalladation. The results presented in this paper provide valuable additional insight into the mechanism of cyclopalladation,[2] which will be discussed based on a study of the N,N-bidentate coordination adducts.

The terdentate aryl C,N,N′ compounds (cis-pincer) reported here are also of more general interest in comparison with organometallic complexes containing the related {N,C,N} ligand $\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}$ (trans-pincer), in which the nitrogen donors adopt a fixed trans position around the metal center. The trans-pincer ligand has been found to stabilize several unusual oxidation states or otherwise transient stages of organometallic reaction pathways.[8] In order to study the effect that changing the nitrogen donors from a fixed trans position to a fixed cis position has on the stabilization of higher oxidation states, we have studied oxidative addition reactions of dihalogens and organic halides to some of the C,N,N′ palladium species discussed here. Some results of initial studies in this field are also reported here.

Results and Discussion

Ligand Synthesis. All ligands (see Chart I) were prepared in one step by reaction of a secondary amine with an alkyl halide, starting from readily available commercial products. Yields are generally low due to extensive quaternization of the tertiary amine function that is also present. Since the desired product is easily separated after basic workup from the nonvolatile quaternary ammonium side product by distillation, this method was used throughout, despite the low yields. The procedures have not been optimized.

Cyclopalladation of Substituted Ethylenediamines and Piperazines. Palladium acetate reacts with an equimolar amount of 2-$RC_6H_4CH_2N(Me)CH_2CH_2NMe_2$ (R = H (**1a**): {CH–N–N}; R = Cl (**1b**), Me (**1c**): {R–CH–N–N}) in methanol at 60 °C to afford the cyclometalated complexes [PdOAc{$C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)$-2-R-3}] ([PdOAc{R-C,N,N′}], see Chart II), which are readily converted to the less soluble halides [PdX{R–C,N,N′}] **2a–e** by metathesis with the appropriate alkali metal salt in good yield (Scheme II).

These terdentate-bound organopalladium compounds are thermally very stable solids (dec temp > 200 °C) which are not air-sensitive. They have only a slight solubility in chlorinated solvents (dichloromethane, chloroform) and are almost insoluble in methanol, acetone, diethyl ether, or hydrocarbons like pentane or benzene. Standard halide

Chart I

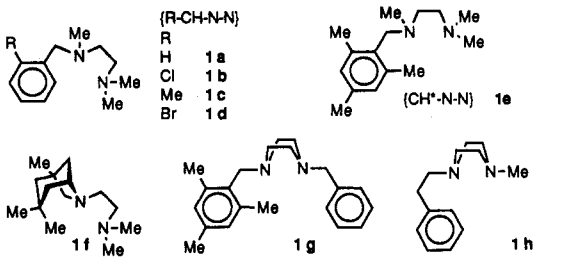
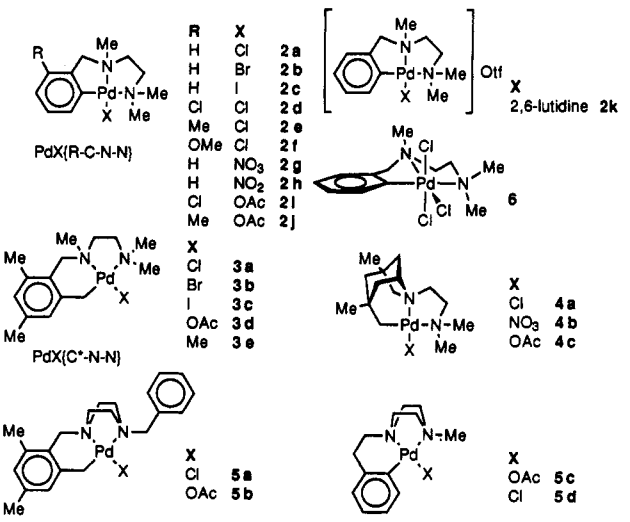
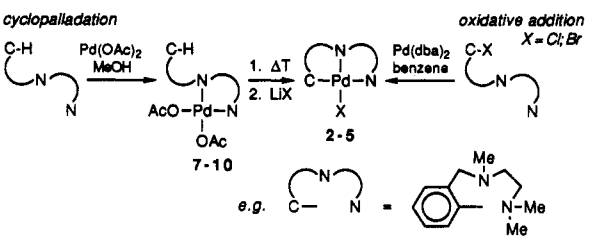


Chart II



Scheme II



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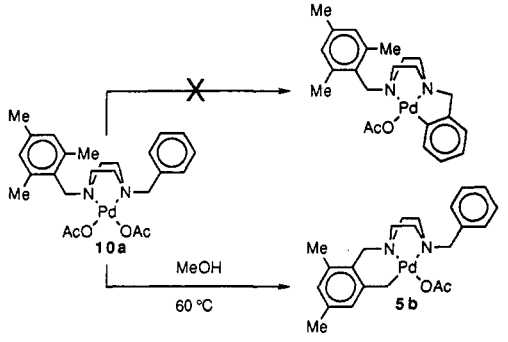
substitution reactions with silver salts can be used for the preparation of nitrate (**2g**) or nitro (**2h**) compounds and for the synthesis of cationic derivatives like the lutidine complex **2k**. The *o*-methoxy derivative **2f** was prepared by treatment of the coordination adduct [$PdCl_2${MeO–CH–N–N}] (obtained by direct methoxylation of **2g**,[1b] see Scheme I) with 2 equiv of $AgNO_3$ and subsequent heating in methanol in the presence of sodium acetate.

Another convenient method for the synthesis of the arylpalladium halides involves oxidative addition of ortho-halogenated organic compounds to $Pd(dba)_2$ (dba = dibenzylidene acetone). In this way, [PdBr{C,N,N'}] (**2b**) can be obtained in almost quantitative yield from {Br–CH–N–N} (**1d**). Even the ortho-chlorinated aryl compound reacts with $Pd(dba)_2$ to give a fair yield (69%) of **2a**, although in this case formation of metallic palladium is an important side reaction. The fact that the oxidative addition of a C–Cl bond proceeds readily at moderate temperature (boiling benzene) in a 1:1 molar ratio of ligand and palladium contrasts with the need of boiling chlorobenzene as solvent in order to effect its (intermolecular) oxidative addition to $Pd(PPh_3)_4$.[9] The much milder condition for the intramolecular oxidative addition of the Ar–Cl bond in **1b** demonstrates that the oxidative addition of a $C(sp^2)$–Cl bond to palladium has a high effective molarity.[10] This also indicates that the nitrogen donors of the ligands probably coordinate to the zero-valent palladium center at some stage of the oxidative addition and thereby lower the energy of the transition state when charge on the palladium center develops.

The *o*-methyl-substituted ligand {Me–CH–N–N} (**1c**), for which in principle both aromatic and benzylic C–H activation might be possible, affords exclusively the aryl derivative **2e** upon cyclometalation. This result emphasises the fact that aromatic C–H bond activation is generally much more facile than aliphatic C–H bond activation[7,11] and is in line with the use of methyl substituents as protective groups of ortho positions that would otherwise be palladated.[12] However, a clean benzylic metalation occurs when both ortho positions are methyl-substituted, as in 2,4,6-$Me_3C_6H_2CH_2N(Me)CH_2CH_2NMe_2$ ({CH*–N–N}, **1e**). The resulting six-membered benzylpalladium compounds obtained after treatment with lithium halides ([PdX{C*–N–N}], **3a–c**) are very stable and not air-sensitive and, in contrast to the arylpalladium complexes, have a good solubility in halogenated solvents. Compound [PdCl{C*–N–N}] can be converted cleanly with methyllithium to the diorganopalladium complex [PdMe{C*–N–N}], which has a high reactivity toward alkyl halides (vide infra).

The utility of the bidentate NCH_2CH_2N bridge in promoting regioselectivity and high-yield conversion in the palladation of a nonactivated aliphatic C–H bond can be found for the functionalized trimethylazabicyclooctane ligand **1f**. Reaction with $Pd(OAc)_2$ in methanol affords the very rigid alkylpalladium compound **4c** (via six-membered ring formation), which is substituted at the *endo*-methyl group and in which the palladium atom is part of a cage that consists of a system of fused five-, six-, and seven-membered rings. The cage moiety of this molecule can be regarded as a heterocyclic, organometallic analogue of tricyclo[4.3.1.$0^{3,8}$]decane (protoadamantane).[13] Apart from the rigidity of the organic backbone, the high stability of the isolated derivatives **4a** and **4b** also probably results from the lack of β-hydrogen atoms. These complexes are extremely soluble in chlorinated solvents.

Scheme III



We also investigated the cyclopalladation of substituted piperazines, in which the nitrogen atoms are connected by two CH_2CH_2 bridges. This greatly reduces the flexibility of the N–N chelate ring and forces the substituents attached to the piperazine unit to adopt a position *in* the square coordination plane around Pd. In order to investigate the effect of this on the preference for aromatic versus benzylic C–H activation, the palladation behavior of ligand **1g** was examined. For this ligand a C–H bond activation competition can be expected between the phenyl ring and the mesityl ring, metalation of the former leading to a five-membered ring and attack on the latter leading to a six-membered chelate ring (Scheme III). Unlike **1c**, for which only aromatic palladation is observed via five-membered ring formation, metalation of **1g** with palladium acetate in methanol results in the formation of the benzylpalladium compound **5b**, even though aromatic palladation is generally much more facile.[6,7,11] To our knowledge, there is only one other example of C–H activation competition where an aliphatic site (leading to a six-membered ring) is activated in preference to an aromatic site (leading to a five-membered ring via cyclopalladation).[6] The preferential benzylic attack in **1g** indicates that the formation of six-membered rings is strongly favored over five-membered rings in piperazine complexes. The ease of six-membered ring formation is also illustrated by the aromatic palladation of a 2-phenylethyl substituent (complexes **5c**, **5d**). A possible reason for the selectivity difference between **1c** (aromatic palladation) and **1g** (benzylic palladation) will be given in the section on the mechanism of cyclopalladation.

The ^1H NMR data of the cyclopalladated piperazines as well as those of the cyclopalladated compounds containing an ethylenediamine unit are presented in Tables I and II. The ^1H NMR data of the cyclopalladated acetate complexes **2i**, **2j**, **3d**, **4c**, and **5b** are those obtained after the nearly quantitative cyclopalladation in CD_3OD solution was complete; i.e., the data are those obtained in the presence of 1 equiv of acetic acid formed during the

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Table I. Selected ^{1}H NMR Data for Cyclopalladated Ethylenediamines 2, 3, and 6[a]

no.	aryl	$ArCH_2N$[f]	$N(CH_2)_2N$	Me[n]	no.	aryl	$ArCH_2N$[f] or $ArCH_2Pd$[h]	$N(CH_2)_2N$[g]	Me[n]
2a[b]	7.46 (m)	4.55 (d)	3.64 (td)[g]	2.89	**3a**[b]	7.06	3.58 (d)	3.31 (td)	2.65
	6.89 (m)[n]	3.67 (d)	3.16 (td)[g]	2.76		6.73	3.40 (d)	2.85 (td)	2.50
			2.63 (m)[m]	2.64			3.22 (d)	2.43 (dd)	2.48
2b[b]	7.66 (d)	4.60 (d)	3.65 (td)[g]	2.89			2.80 (d)	2.36 (dd)	2.25
	6.91 (m)[n]	3.68 (d)	3.18 (td)[g]	2.76					2.24
			2.65 (m)[m]	2.67	**3b**[b]	7.06	3.52 (d)	3.24 (td)	2.74
2c[b]	8.02 (d)	4.67 (d)	3.67 (td)[g]	2.84		6.71	3.38 (d)	2.83 (td)	2.51
	6.85 (m)[n]	3.70 (d)	3.20 (td)[g]	2.75			3.33 (d)	2.38 (dd)	2.48
			2.60 (m)[m]	2.73			2.76 (d)	2.29 (dd)	2.26
2d[c]	7.38 (dd)	4.46 (d)	3.66 (td)[g]	2.93					2.25
	6.95 (dd)	4.13 (d)	3.17 (td)[g]	2.77	**3c**[c]	7.06	3.48 (d)	3.17 (td)	2.83
	6.86 (td)		2.66 (m)[m]	2.65		6.70	3.36 (d)	2.82 (td)	2.52
2e[b]	7.30 (d)	4.37 (d)	3.65 (td)[g]	2.90			3.63 (d)	2.37 (dd)	2.43
	6.83 (t)	3.84 (d)	3.15 (td)[g]	2.75			2.58 (d)	2.29 (dd)	2.28
	6.74 (d)		2.64 (m)[m]	2.64					2.25
				2.16	**3d**[d,i]	6.92	3.70 (d)	3.43 (td)	2.49
2f[b]	7.06 (d)	4.27 (d)	3.63 (td)[g]	2.71		6.73	3.45 (d)	2.94 (td)	2.48
	6.89 (t)	4.02 (d)	3.13 (td)[g]	2.89			2.97 (d)	2.45[l,m]	2.39
	6.50 (d)		2.58 (m)[m]	2.73			2.45[l]		2.24
				2.62					2.22
2g[b]	6.90 (m)[o]	4.52 (d)	3.61 (td)[g]	2.93	**3e**[e,k]	7.24	3.35 (d)	2.58 (td)	2.19
		3.66 (d)	3.13 (td)[g]	2.78		6.64	3.18 (d)	2.00 (td)	2.15
			2.64 (m)[m]	2.61			3.10 (d)	1.44 (dd)	1.95
2h[b]	7.17 (m)	4.50 (d)	3.60 (td)[g]	2.87			2.79 (d)	1.35 (dd)	1.93
	6.90 (m)[n]	3.59 (d)	3.17 (td)[g]	2.79					1.87
			2.64 (m)[m]	2.64					
2i[d,i]	6.92 (d)	4.50 (d)	3.73 (td)[g]	2.88					
	6.79 (t)	4.03 (d)	3.21 (td)[g]	2.69					
	6.63 (d)		2.62 (m)[m]	2.48					
2j[d,i]	6.70 (m)[m]	4.37 (d)	3.70 (td)[g]	2.83					
	6.50 (t)	3.83 (d)	3.20 (td)[g]	2.66	**6**[b]	7.59 (d)	5.45 (d)[f]	4.61 (td)	2.98
			2.62 (m)[m]	2.47		7.17 (t)	3.47 (d)[f]	3.51 (td)	2.90
				2.15		7.06 (t)		2.89[l]	2.88
2k[b,j]	6.93 (m)[m]	4.69 (d)	3.84 (td)[g]	2.93		6.94 (d)		2.63 (dd)	
	6.67 (dt)	3.78 (d)	3.45 (td)[g]	2.65					
	5.71 (d)		2.88 (dd)[g]	2.38					
			2.74 (dd)[g]						

[a] Signals are singlets and integrate for one proton unless denoted otherwise. [b] 200 MHz; $CDCl_3$. [c] 300 MHz; $CDCl_3$. [d] 200 MHz; CD_3OD. [e] 300 MHz; C_6D_6. [f] $J \approx 13$ Hz. [g] $J \approx 14$ and 3 Hz. [h] $J \approx 9$ Hz. [i] Acetate CH_3 at ca. 1.9 ppm. [j] Lutidine: 7.77 (t), 7.37 (d), 7.26 (d), 3.31, 3.00 ppm. [k] PdMe: 0.40 ppm. [l] Multiplicity not clear as signal is hidden under other signals. [m] Integral: two hydrogens. [n] Integral: three hydrogens. [o] Integral: four hydrogens. [p] $ArCH_2N$.

cyclopalladation. The acetate complex **5c** has been isolated. Assignments for the cyclopalladated compounds **4** are based on 2-D ^{1}H,^{1}H and ^{13}C,^{1}H correlation NMR measurements on the complexes **4a** and **4b**. The ^{1}H NMR spectra of the piperazine complexes show very broad resonances for the N–N chelate ring protons (probably a result of slow wagging of this unit) that sharpen somewhat at 60 °C. Most compounds have also been characterized by ^{13}C NMR and IR spectroscopy, and elemental analysis.

Reactions with Electrophiles: Dihalogens and Alkyl Halides. NMR spectra recorded immediately after bubbling Cl_2 through a $CDCl_3$ solution of **2a** showed the total consumption of the starting material and the appearance of two new compounds, the minor component (<20%) being identified as the product formed by chlorination of the Pd–C bond, i.e., $[PdCl_2\{Cl–CH–N–N\}]$ (**7b**). This coordination adduct (Chart III) was independently prepared from the free ligand 2-ClC_6H_4-$CH_2N(Me)CH_2CH_2NMe_2$ and Li_2PdCl_4. The product **7b** is also obtained (but in quantitative yield) by chlorination of **2a** in 1,2-dichloroethane, followed by heating the solution under reflux.[14] The major component shows a well-defined first-order pattern in the aromatic region and two well-defined double triplets, originating from two NCH_2CH_2N protons, that are characteristic of cyclopalladated complexes containing an {R–C,N,N'} ligand (Table I). This product is quite unstable and decomposes slowly in solution in the course of several hours. Therefore, no attempts have been made to isolate it.

The above observations point to an oxidative addition of Cl_2 to **2a**, resulting in an octahedral Pd(IV) complex **6** which is sufficiently stable at room temperature to be identified by means of NMR spectroscopy (Table I). The unusual stability of this (trichloro)(aryl)palladium(IV) complex[15] is very likely due to the strongly electron-donating {C,N,N'} ligand; it is known that the Pd(IV) state is well stabilized by bidentate nitrogen ligands (N–N) in compounds of the type $PdCl_2Y_2$(N–N) (Y = C_6F_5, Cl; N–N = en, bpy, or phen).[16] This stabilization of high oxidation states by the {C,N,N'} ligand is reminiscent of the stabilizing effect that the isomeric $\{C_6H_3(CH_2NMe_2)_2$-2,6} ({N–C–N}) ligand has on high oxidation states, e.g., Ni(III) and Pt(IV).[8] In principle, the present C,N,N' octahedral compounds can exist in two isomeric forms; i.e., the molecule might adopt either the *fac*- or the *mer*-configuration (Figure 1).[17]

(14) Although **6** decomposes at room temperature to give inter alia **7b**, this decomposition is not clean, probably as a result of excess dissolved dichlorine. A much cleaner formation of **7b** results when this excess is removed by boiling the solution.

(15) No evidence for the formation of a tetravalent Pd(IV) intermediate could be found in the reaction of terdentate-bound cyclopalladated azobenzene derivatives with dichlorine. Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *J. Organomet. Chem.* **1991**, *414*, 421.

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Table II. Selected ^{1}H NMR Data for Cyclopalladated Ethylenediamines 4 and Piperazines 5[a]

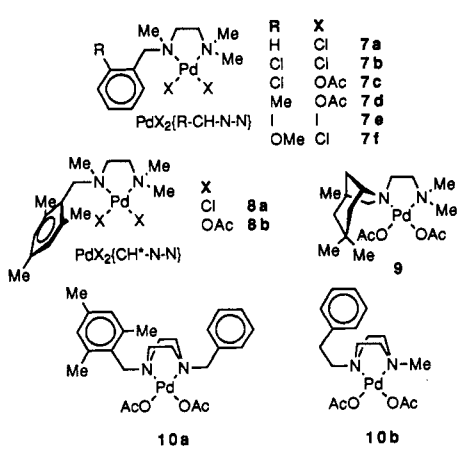
no.	NCH	CCH	$PdCH_2$	Me[p]
4a[d]	4.61 (dd)[g]	2.28 (dd)[k]	2.19 (dd)[g]	2.56
	3.06 (t)[h]	1.65 (m)	1.31 (dd)[g]	2.47
	3.01 (ddd)[i]	1.50 (d)[l]		0.98
	2.69 (ddd)[j]	1.37 (m)[n]		0.97
	2.57[n]			
	2.53 (dd)[g]			
	2.38 (ddd)[j]			
4b[d]	4.65 (dd)[g]	2.35 (dd)[k]	1.95 (dd)[g]	2.53
	3.04 (t)[h]	1.66 (m)	1.37[n]	2.48
	3.00 (ddd)[i]	1.50 (d)[l]		0.98
	2.72 (ddd)[j]	1.37 (m)[q,t]		0.94
	2.60[n]			
	2.56 (dd)[g]			
	2.40 (ddd)[j]			
4c[e,f,m]	4.66 (dd)[g]	2.36 (dd)[k]	1.72 (dd)[g]	2.46
	3.12 (t)[h]	1.74 (m)	1.28 (dd)[g]	2.44
	3.07 (ddd)[i]	1.43 (m)[q]		1.00
	2.77 (ddd)[j]			0.95
	2.64 (dd)[g]			
	2.62[n]			
	2.47[n]			

no.	aryl	$ArCH_2$[o]	pip[b]	Me[p]
5a[c,f]	7.28 (m)[r]	3.93	3.40 (m)[q]	2.24
	7.10	3.35	2.36 (m)[q]	2.21
	6.71	3.18		
5b[e,f,m]	7.29 (m)[r]	3.76	3.40 (m)[q]	2.21[s]
	6.96	3.31	2.50 (m)[o]	
	6.72	2.89	2.28 (m)[o]	

no.	aryl	pip[b,o]	$N(CH_2)_2Ar$[h,o]	Me[p]
5c[c,f,m]	7.26 (d)	3.91 (m)	2.98 (bt)	2.57
	6.90 (m)[o]	3.76 (m)	2.49 (t)	
	6.80 (m)	2.61 (m)		
		2.43 (m)		
5d[d,f]	7.85 (dd)	3.88 (b)	3.01 (b)	2.58
	6.86 (m)[p]	3.52 (m)	2.52 (t)	
		2.64 (b)		
		2.48 (m)		

[a] Signals are singlets and integrate for one proton unless denoted otherwise. [b] pip = $N(CH_2CH_2)_2N$. [c] 200 MHz; $CDCl_3$. [d] 300 MHz; $CDCl_3$. [e] 200 MHz; CD_3OD. [f] At 60 °C. [g] $J \approx 10$ and 2 Hz. [h] $J \approx 5$ Hz. [i] $J \approx 13$, 10, and 3 Hz. [j] $J \approx 13$, 5, and 3 Hz. [k] $J \approx 12$ and 5 Hz. [l] $J \approx 14$ Hz. [m] Acetate CH_3: 1.95 ppm (for **4c**); 2.05 ppm (for **5c**). [n] Multiplicity not clear as signal is hidden under other signals. [o] Integral: two hydrogens. [p] Integral: three hydrogens. [q] Integral: four hydrogens. [r] Integral: five hydrogens. [s] Integral: six hydrogens. [t] Integral includes one hydrogen of the $PdCH_2$ group.

Chart III



In the *fac*-configuration one of the methyl groups is placed almost above the aryl ring. This should result in a significant upfield ^{1}H NMR shift for this methyl group compared to the other methyl group attached to the same nitrogen atom.[18] Therefore, since in the NMR spectra the three methyl groups of the {C,N,N'} ligand are nearly equivalent, we propose the *mer*-configuration for these Pd(IV) complexes. The formation of **6** from **2a** probably involves an S_N2-type mechanism. The process is initiated by end-on coordination of Cl_2 (as observed for I_2 in [PtI(η^1-I_2){N-C-N}]), followed by loss of Cl^- and subsequent trans addition of the latter to the square-pyramidal cationic Pd(IV)-intermediate (Figure 2).[19] Other mechanisms, such as a concerted cis addition, cannot be excluded, however, and further studies to clarify this point are current.

Figure 1. Possible *mer* (left) and *fac* (right) orientation of the {C,N,N'} ligand in the octahedral Pd(IV) complex **6**.

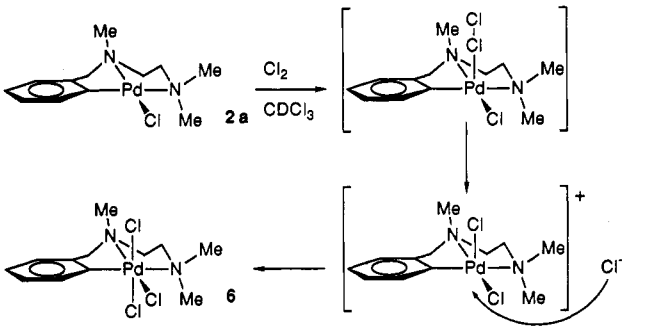


Figure 2. Suggested mechanism for oxidative addition of dichlorine to **2a**.

Necessarily, the platinum(IV) compound [$PtCl_3${NCN}][20] also has a *mer*-arrangement of the chlorine atoms. In the reaction of I_2 with **2c**, the coordination adduct [PdI_2{I-CH-N-N}] (**7e**) only was formed instantaneously, and, in marked contrast to the oxidative addition of dichlorine, no Pd(IV) complexes were identified.

The diorganocomplex [PdMe{C*-N-N}] (**3e**), but not the monoorgano complexes [PdCl{C*-N-N}] (**3a**) or [PdCl{C,N,N'}] (**2a**), reacts cleanly with methyl iodide in acetone-d_6 at room temperature to give [PdI{C*-N-N}] (**3c**) and ethane as the only products detected by ^{1}H NMR. No product derived from C-C coupling to the {C*-N-N} unit is formed. An intermediate species could be detected when the reaction was monitored by ^{1}H NMR at low temperature (-30 °C) in acetone-d_6. This species shows resonances at 1.49 and 1.06 ppm, which can be ascribed to Pd(IV)Me groups that have resulted from an oxidative addition. Since the spectrum is complex due to the absence of symmetry in this, probably octahedral, Pd(IV) complex,[21] the exact structure of this intermediate has not

(17) A *fac*-coordination mode of the {C,N,N'} ligand has recently been found in a pentacoordinated iridium complex. Wehman-Ooyevaar, I. C. M.; Kapteijn, G. M.; van Koten, G. Submitted for publication.

(18) Such a shielding of an NMe group is observed in platinum(IV) complexes of the type *cis,cis*-$PtX_2(CN)_2$, where CN is 2-[(*N,N*-dimethylamino)methyl]phenyl or 8-(*N,N*-dimethylamino)naphthalene. van Beek, J. A. M.; van Koten, G.; Wehman-Ooyevaar, I. C. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 883.

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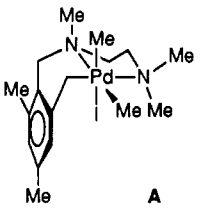
Table III. Selected Structural Data with Esd's in Parentheses for 2c and 3c

2c		3c	
	Bond Lengths (Å)		
Pd–C(1)	1.999(6)	Pd–C(7)	2.027(3)
Pd–I	2.5925(5)	Pd–I	2.5957(3)
Pd–N(1)	2.065(4)	Pd–N(1)	2.115(2)
Pd–N(2)	2.193(4)	Pd–N(2)	2.2167(19)
		C(1)–C(7)	1.477(4)
	Bond Angles (deg)		
I–Pd–N(1)	174.81(10)	I–Pd–N(1)	178.44(7)
C(1)–Pd–N(1)	82.82(18)	C(7)–Pd–N(1)	87.20(10)
N(1)–Pd–N(2)	84.42(15)	N(1)–Pd–N(2)	83.70(9)
Pd–N(1)–C(10)	114.0(3)	Pd–N(1)–C(11)	110.98(16)
		Pd–C(7)–C(1)	103.76(17)
	Dihedral Angles (deg)		
C(2)–C(1)–Pd–I	27.5(5)	C(1)–C(7)–Pd–I	114.72(16)
C(1)–Pd–N(1)–C(10)	82.7(4)	C(7)–Pd–N(1)–C(11)	–96.9(2)
N(1)–C(8)–C(9)–N(2)	58.3(5)	N(1)–C(12)–C(13)–N(2)	–56.6(3)
I–Pd–N(2)–C(9)	–179.0(3)	I–Pd–N(2)–C(13)	–179.44(19)

been elucidated unambiguously. However, we propose structure A for this complex, in analogy with the closely



A

related noncyclometallated Pd(IV) intermediate [PdBr-$Me_2(CH_2Ph)$(tmeda)] (tmeda = *N,N,N',N'*-tetramethylethane-1,2-diamine), which also eliminates ethane upon warming, although somewhat less selectively.[22]

A clean reaction was also observed between [PdMe{C*–N–N}] and acetyl chloride in benzene. Again, the terdentate {C*–N–N} ligand was unaffected by this reagent, and acetone together with [PdCl{C*–N–N}] were the only products detected by ^1H NMR spectroscopy. The robustness of the {C*–N–N} skeleton in these reactions makes complexes of the type [PdX{C*–N–N}] good candidates for catalysts of C–C coupling reactions between organic halides and mild alkylating organometallics in a Pd(II)–Pd(IV) cycle.[23] The above results indicate that the {C,N,N'} and {C*–N–N} ligands are able, like the {N–C–N} ligand with trans-positioned amine groups, to stabilize high oxidation states.

Molecular Structures of [PdI{C_6H_4-($CH_2N(Me)CH_2CH_2NMe_2$)-2}] (2c) and of [PdI-{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (3c). Single-crystal X-ray diffraction structures of the iodide complexes **2c** and **3c** were determined in order to compare their structural features with those of the noncyclopalladated compound *cis*-[PdI(C_6H_5)(tmeda)][24] and the N–C–N terdentate arylpalladium compound [PdI{C_6H_3-(CH_2NMe_2)$_2$-2,6}]·$2I_2$.[8] Relevant bond distances and bond angles are given in Table III. ORTEP drawings with the adopted numbering schemes are shown in Figure 3.

In the molecules of **2c** and **3c** the palladium coordination spheres show no unusual features, other than the Pd–N(1) bond of 2.065(4) Å in **2c**, which is markedly shorter than the analogous Pd–N bond of 2.127(6) Å in [PdI-(C_6H_5)(tmeda)].[24] This shortening is most likely caused by the ring strain within the two fused five-membered ring systems.[25,26] The other bond lengths are in their normal ranges, when account is taken of the different trans influences of (anionic) carbon donors and (neutral) amine ligands. The NCH_2CH_2N bridges show the characteristic staggered conformation. In both compounds, the N(1)–Me group adopts a notable "axial" position with respect to the square planar coordination plane around palladium.

Molecular Structure of [PdI_2{2-I-C_6H_4-($CH_2N(Me)CH_2CH_2NMe_2$)-2}] (7e). We have attempted to obtain single crystals of the palladium acetate coordination adducts in order to see whether X-ray diffraction provides some information about the approach of C–H bonds that can be palladated toward the metal center. Unfortunately, these real precursors of the cyclometalated products proved very hard to crystallize. However, we have been able to obtain single crystals of the related diiodide compound **7e**, whose NMR spectrum indicates it to have a structure similar to that of the $Pd(OAc)_2$ coordination adducts of 2-substituted {R–C,N,N'} ligands; NMR spectra of these coordination adducts are discussed below.

The molecular structure together with the adopted numbering scheme is shown in Figure 4, and important bond angles and bond distances are collected in Table IV.

The coordination sphere around palladium is approximately square planar, but is slightly distorted toward a tetrahedral geometry. The organic ligand is bidentate bound through the two nitrogen atoms. One of the iodine atoms, I(1), and the palladium center are involved in a short intramolecular contact with the ortho proton, the C–H(ortho) bonding vector pointing towards the iodine (I(1)–H(ortho) = 3.02(2) Å; Pd–H(ortho) = 2.97(2) Å). Although these distances are too long to indicate any significant bonding, they are both substantially shorter than the sum of the van der Waals radii (r_{I+H} = 3.4 Å; r_{Pd+H} = 3.1 Å).[27] The observed structure is reminiscent of that of *trans*-dichloro-bis(azobenzene)palladium(II),

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(26) Markies, B. A.; Wijkens, P.; Boersma, J.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 133.

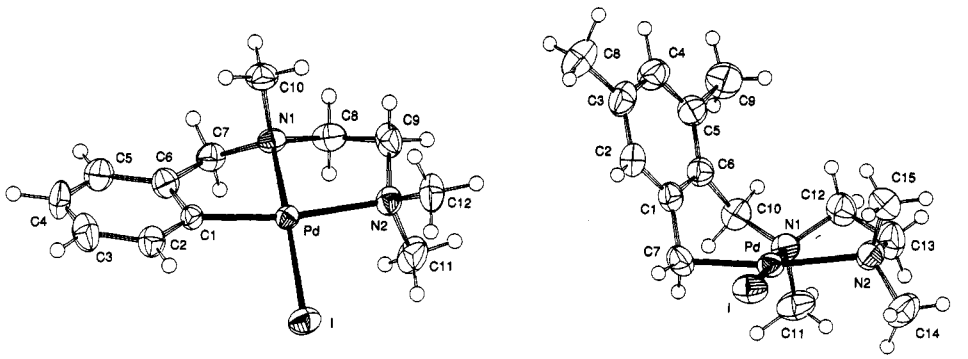

Figure 3. ORTEP drawings (50% probability level) of the molecular structures of [PdI{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (**2c**) (left) and [PdI{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (**3c**) (right) together with the adopted numbering scheme.

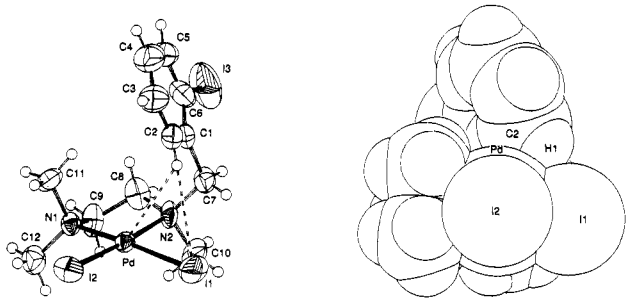

Figure 4. ORTEP drawing (left; 50% probability level) and space-filling model (right; view along the I(2)–Pd bond) of the molecular structure of [PdI_2{2-I-$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (**7e**) together with the adopted numbering scheme.

Table IV. Selected Structural Data with Esd's in Parentheses for 7e

	Bond Lengths (Å)		
Pd–I(1)	2.5865(14)	I(1)–H(1)	3.023(15)
Pd–I(2)	2.5833(16)	Pd–H(1)	2.968(15)
Pd–N(1)	2.105(9)	Pd–C(2)	3.405(15)
Pd–N(2)	2.132(11)		
	Bond Angles (deg)		
I(1)–Pd–I(2)	88.86(4)	I(1)–Pd–N(1)	175.2(3)
N(1)–Pd–N(2)	84.7(4)	I(2)–Pd–N(2)	176.0(3)
	Dihedral Angles (deg)		
N(2)–C(8)–C(9)–N(1)	54.80(16)	I(1)–Pd–N(2)–C(8)	−177.7(8)
C(1)–C(7)–N(2)–Pd	−60.60(12)	I(2)–Pd–N(1)–C(9)	−163.1(8)

which also contains a ligand that is prone to cyclometalation. In this case too the ortho hydrogen is positioned between the chlorine and palladium atom.[28] Such a position is not always encountered in square-planar complexes in which a ligand proton makes a close approach to the metal. In fact, a much more common approach is that in which the hydrogen atom is positioned perpendicularly above the metal center.[29] Although the distance between the ortho carbon atom and the Pd center found in the structure of **7e** (3.405(15) Å) does not permit a description as a Wheland-type intermediate,[30] one might wonder whether a triangular, oblique arrangement is typical for aromatic ligands that readily cyclometalate. Starting from this arrangement, the ortho proton could be easily split off (as HX), while the ortho carbon atom's positioning, perpendicularly above the metal, allows an electrophilic attack by palladium(II). The significance of the position of the aryl ring with respect to the square coordination plane around palladium will be discussed in the concluding section.

Mechanism of the Cyclopalladation. In order to obtain more insight into the mechanism of cyclopalladation of the bidentate ligands described in this work, we have prepared several coordination adducts of the type *cis*-[PdX_2{CH–N–N}] and studied their structure and cyclopalladation in solution by means of NMR. The advantage of this approach is that such substituted ethylenediamines and piperazines form well-defined monomeric coordination adducts with palladium salts.[31] This contrasts with the complex series of equilibria observed during the cyclopalladation of coordination adducts of *N,N*-dimethylbenzylamine, where the nature of several of the species involved is unclear.[32] In particular, questions arise as to whether cyclometalation is initiated by decoordination of one of the nitrogen atoms or by loss of an anion, resulting in the formation of a kinetically active 14 electron species, or whether, perhaps, a 16-electron species itself is active. A further question is which factors determine the preference for six-membered ring formation by benzylic attack vs five-membered ring formation by aromatic attack in **1g** and the reversed preference observed for **1c**. A detailed study of the NMR spectra of the coordination complexes was carried out in order to find an answer to these questions.

Whether cyclopalladation occurs or not proved to be strongly dependent on the nature of the anion X and the solvent. Total inhibition of the cyclopalladation was observed in the case of chloride anions. For example, after heating the complex *cis*-[$PdCl_2${$C_6H_5CH_2N(Me)CH_2CH_2NMe_2$}] ([$PdCl_2${CH–N–N}]) (**7a**) for 24 h in methanol under reflux (in the absence of base), only the starting material was recovered, and therefore, further studies were concentrated on the palladium acetate adducts.

(27) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Pauling, L. *Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, 1944; p 189.

(28) Khare, G. P.; Little, R. G.; Veal, J. T.; Doedens, R. J. *Inorg. Chem.* **1975**, *14*, 2475.

(29) For a comprehensive article with many references on this subject: Albianati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812.

(30) In neutral or cationic palladium or platinum complexes with an η^1-coordinated aryl group, the M–Aryl distance ranges from 2.18 to 2.34 Å. (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891. (c) Falvello, L. R.; Forniés, J.; Navarro, R.; Sicilia, V.; Tomás, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 891.

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(32) (a) Jones, T. C.; Nielson, A. J.; Rickard, C. E. *Aust. J. Chem.* **1984**, *37*, 2179. (b) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629.

The $Pd(OAc)_2$ coordination adducts **7c**, **7d**, and **8b** are fairly unstable and cyclometalate slowly even in the solid state. They were characterized with ^1H NMR and IR spectroscopy and, in the case of **7c** (which was sufficiently stable for elemental analysis), also by ^{13}C NMR spectroscopy. The related dihalide coordination adducts **7b** and **8a**, whose NMR spectra indicate that they have a structure similar to that of the $Pd(OAc)_2$ adducts, have both been characterized by spectroscopic methods and elemental analysis. Complexes **9**, **10a**, and **10b** were generated by dissolution of accurately weighed 1:1 mixtures of $Pd(OAc)_2$ and ligand in CD_3OD; the complexes were characterized in situ. ^1H NMR data of the coordination adducts are presented in Table V.

The cyclopalladation of the $Pd(OAc)_2$ coordination adducts **7c**, **7d**, and **8b** was followed by ^1H NMR spectroscopy in CD_3OD solution at 60 °C, and these complexes were found to convert cleanly and almost quantitatively into their cyclometalated derivatives **2i**, **2j**, and **3d**, respectively. No intermediates were detected. Evidence for rigid nitrogen donor coordination of the $ArCH_2N(Me)CH_2CH_2NMe_2$ unit at 60 °C (the temperature at which cyclopalladation occurs) is provided, firstly, by the presence of a well-defined AB pattern of the benzylic CH_2 group, indicating chirality of the adjacent nitrogen atom as a result of its coordination to the metal center, and, secondly, by the presence of three distinct resonances of the NMe groups, indicating that the nitrogen atom of the CH_2NMe_2 group also remains coordinated to the metal center. In marked contrast to the result with methanol as solvent, no reaction occurred when a $CDCl_3$ solution of **7c** was heated for 18 h at 60 °C. This solvent effect, combined with the evidence for rigid N donor coordination, strongly suggests that cyclopalladation is initiated by loss of an acetate anion; the latter being only possible in a polar, ionizing solvent like methanol. This is also in agreement with the inertness of **7a** toward cyclopalladation since chloride anions are more tightly bound to palladium than acetate ions. Probably, benzylic C–H activation is also initiated by loss of an acetate anion as the dichloride coordination adduct **8a** does not cyclopalladate to any extent, not even when heated under reflux in 1,2-dichloroethane for 4 days; after workup, only starting material was recovered. The cyclopalladation in CD_3OD of the coordination adducts **9**, **10a**, and **10b** was also followed by ^1H NMR spectroscopy. In all cases, straightforward conversion to the cyclometalated products was observed and no intermediates were detected.

There is a noteworthy difference in the ^1H NMR spectra of the PdX_2 coordination adducts (X = acetate or halide) of substituted ethylenediamines ({R–CH–N–N} and {CH*–N–N} ligands) and those of piperazines (**1g** and **1h**); the spectra of the ethylenediamine complexes indicate a close approach of certain CH bonds toward the metal center, whereas the spectra of the piperazine complexes give no indication for this. The close approach toward the metal center is most evident for the PdX_2{R–CH–N–N} coordination adducts (**7a–7e**), which show a very large downfield shift of the aromatic ortho proton ($\delta \approx 9.3$ ppm; $\Delta\delta \approx 2$ ppm). The low-field shift results from the magnetic anisotropy of the metal center and indicates that this proton is held above-plane close to the metal.[29,33] This downfield shift persists at 60 °C (in CD_3OD) and even above 100 °C in DMSO-d_6, which (like methanol) turned out to be a very good solvent for the cyclopalladation of **7c**. A less remarkable, but still significant shift ($\Delta\delta \approx 7$ ppm) is observed too for the ortho carbon atom in the ^{13}C spectrum of **7c**. The approach of the ortho proton to the palladium center in solution is very likely to be similar to that found in the solid-state crystal structure of **7e**; i.e., the proton is positioned over the Pd–X bond (Figure 4).

Further information as to whether the structure observed in the solid state for **7e** is retained in solution can be obtained from a conformational analysis of the NCH_2-CH_2N skeleton based on ^1H NMR H–H coupling data. The spectrum of the diiodide coordination adduct **7e** was

Table V. Selected ^1H NMR Data for Coordination Adducts 7–10[a]

no.	aryl	$ArCH_2N^i$	$N(CH_2)_2N$	Me^p
7a[c]	8.15 (dd)	4.84 (d)	2.98 (m)[o]	3.10
	7.49 (m)[p]	3.23 (d)	2.18 (m)[o]	2.72
				2.22
7b[d]	9.32 (dd)	4.77 (d)	3.00 (td)[j]	3.13
	7.61 (td)	3.72 (d)	2.88 (td)[j]	2.70
	7.45 (m)[o]		2.34 (dt)[j]	2.20
			2.20 (dt)[j]	
7c[e,m]	9.25 (d)	4.13 (d)	2.96 (m)[o]	2.87
	7.67 (m)	3.75 (d)	2.30 (m)[o]	2.43
	7.52 (m)[o]			2.13
7d[e,m]	9.25 (d)	4.05 (d)	2.84 (m)[o]	2.86
	7.56 (t)	3.45 (d)	2.22 (m)[o]	2.40
	7.37 (t)			2.37
	7.28 (d)			2.06
7e[d]	9.47 (dd)	5.24 (d)	3.02 (td)[j]	3.27
	7.94 (dd)	3.96 (d)	2.88 (td)[j]	2.95
	7.60 (td)		2.42 (dt)[j]	2.29
	7.14 (td)		2.12 (dt)[j]	

no.	NCH	NMe^p	CCH	CMe^p
9[e,m]	4.45 (b)	2.69	2.34 (dd)[k]	1.15
	3.52 (td)[k]	2.43	2.00 (d)[i]	1.03
	3.09 (d)[i]		1.47 (m)[q]	0.92
	2.84 (m)[o]			
	2.57 (d)[i]			
	2.50[n]			

no.	aryl	$ArCH_2N^i$	$N(CH_2)_2N^o$	Me^p
8a[c,g]	6.96[o]	4.79 (d)	~2.8 (vb)	3.08
		4.18 (d)	2.33 (m)	2.78
				2.75 (b)[s]
				2.58
				2.27
8b[e,h,m]	7.02	4.42 (d)	2.90 (b)	2.89
	6.94	3.93 (d)	~2.4 (b)	2.71
				2.47
				2.45
				2.38
				2.24

no.	aryl	$ArCH_2N^o$	pip^b	Me
10a[e,m]	7.34 (m)[r]	4.07	4.07 (m)[o]	2.35[s]
	6.87[o]	3.84	3.89 (m)[o]	2.19[p]
			2.10 (m)[q]	

no.	aryl	pip^b	$N(CH_2)_2Ar^o$	Me^p
10b[f,m]	7.22 (m)[r]	3.98 (m)[o]	2.92 (m)	2.25
		3.86 (m)[o]	2.68 (m)	
		2.45 (m)[q]		

[a] Signals are singlets and integrate for one proton unless denoted otherwise. [b] pip = $N(CH_2CH_2)_2N$. [c] 200 MHz; $CDCl_3$. [d] 300 MHz; $CDCl_3$. [e] 200 MHz; CD_3OD. [f] 300 MHz; CD_3OD. [g] At 60 °C. [h] At −20 °C. [i] $J \approx 13$ Hz. [j] $J \approx 12$ and 4 Hz. [k] $J \approx 13$ and 4 Hz. [l] $J \approx 16$ Hz. [m] Acetate CH_3 at ca. 1.9 ppm. [n] Multiplicity not clear as signal is hidden under other signals. [o] Integral: two hydrogens. [p] Integral: three hydrogens. [q] Integral: four hydrogens. [r] Integral: five hydrogens. [s] Integral: six hydrogens.

(33) Miller, R. G.; Stauffer, R. D.; Fahey, D. R.; Parnell, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 1511.

sufficiently well-resolved (after resolution enhancement by Gaussian multiplication) for the vicinal coupling constants ^3J(H,H) to be determined from the NCH_2CH_2N multiplet resonances. This allows the determination of the equilibrium constant for the $\lambda \rightleftharpoons \delta$ equilibrium by a conformational analysis based on Karplus equations (see addendum).[34] Since **7e** is chiral, there are two enantiomers present in solution, and these will have a reversed preference for either the λ- or the δ-conformation of the NCH_2CH_2N skeleton. The crystal structure of **7e** shows that (*R*)-**7e** has the δ-conformation in the solid state (Figure 4). At 25 °C, the mole fraction n_δ of (*R*)-**7e** adopting the δ-conformation is 0.84 ± 0.05, and this value decreases only slightly to n_δ = 0.78 ± 0.05 upon increasing the temperature to 60 °C. Thus, both the low-field shift of the ortho proton and the conformational analysis of the NCH_2CH_2N resonances indicate that the structure of **7e** in the solid state is retained to a large extent in solution, even at 60 °C, the temperature at which cyclopalladation occurs for palladium acetate coordination adducts.

A smaller downfield shift was found for both ortho protons of **7a** (δ = 8.18 ppm; $\Delta\delta \approx 1$ ppm), suggesting that the aryl ring in this complex is rotating freely around the Ph–CH_2 axis whereas in the 2-substituted complexes **7a**–**7e** this rotation is blocked. However, slow rotation was observed for the more sterically hindered bis-ortho-substituted [$PdCl_2${CH*–N–N}] (**8a**) and [$Pd(OAc)_2${CH*–N–N}] (**8b**). At room temperature, the two *o*-methyl groups are not visible in the NMR spectra of these compounds, being hidden as a very broad signal under the other aliphatic resonances, and only one signal is observed in the aromatic region. For **8b**, upon lowering the temperature to −20 °C one observes two separate signals for the aromatic protons and six distinct singlets for the methyl groups. A large difference in chemical shift is found for the two *o*-methyl substituents, one having a normal value of 2.40 ppm, whereas the other is markedly shifted to low field (2.90 ppm; $\Delta\delta \approx 0.5$ ppm) and is apparently positioned above the metal center of the square coordination plane.[35] At higher temperature, the two signals coalesce to a broad singlet at 2.67 ppm. Thus, rotation of the aryl ring (on the NMR time scale) is observed for the nonsubstituted complex **7a** and for the bis-ortho-substituted complexes **8a** and **8b**, but not for the mono-ortho-substituted complexes **7a**–**7e**.

The ^{1}H NMR spectrum of the piperazine coordination adduct **10a** does not show any slow rotation of the mesityl group as observed for **8a** and **8b** at room temperature; the *o*-methyl groups resonate as a sharp singlet at 2.35 ppm, and there is only one sharp singlet for the two aromatic protons of the mesityl unit. No downfield shifts of the ortho protons of the phenyl group are observed for **10a**. Downfield shifts of the ortho protons are also absent in the ^{1}H NMR spectrum of the piperazine coordination adduct **10b**. Thus, in contrast to the ethylenediamine coordination adducts, there are no interactions between the aryl units and the metal center in the piperazine complexes **10a** and **10b**.[36]

Conclusions

A number of new, rigid terdentate C,N,N'-bound aryl-, benzyl-, and alkylpalladium complexes have been prepared via direct palladation of the initially bidentate N,N-coordinated ligands. This bidentate coordination limits the degree of freedom of the ligand around the coordination sphere of the metal and allows one to direct the cyclopalladation selectively toward sp^2 or sp^3 C–H activation and toward five-membered or six-membered ring formation. Some initial studies demonstrate that the behavior of Pd(II) complexes in oxidative addition/reductive elimination reactions can be controlled by coordination of palladium to such rigid terdentate C,N,N' bound ligands. This is exemplified by the detection of the unusually stable organometallic Pd(IV) dichlorine adduct **6** and by the use of the {C*–N–N} group as spectator ligand in reactions of [PdMe{C*–N–N}] with methyl iodide and acetyl chloride. Complex **6** represents, to our knowledge, the first spectroscopically characterized organometallic Pd(IV) dihalogen adduct that does not have highly electronegative pentafluorophenyl substituents.[16a]

A study of the bidentate coordination adducts has given insight into the mechanism of the cyclopalladation reaction. Cyclopalladation probably proceeds via an electron-deficient cationic 14-electron species, which is formed by dissociation of an acetate anion in a polar solvent. For the cyclopalladation of *aryl* rings, evidence has been found that the formation of this 14-electron species is preceded by an oblique, above-plane approach of the ortho C–H bond toward an anionic ligand. This positioning is observed in the crystal structure of the coordination adduct **7e**, and ^{1}H NMR spectra of coordination adducts of the type [PdX_2{R–CH–N–N}] indicate that this position is to a large degree retained in solution.

It has been suggested that an axial approach of a hydrogen atom toward a square-planar d^8 metal center is destabilizing.[37] This conclusion is based on coordination adducts where the steric constraints of the system force the interacting C–H bond to adopt a specific position with respect to the metal center. Such steric constraints are absent in [PdX_2{R–CH–N–N}] coordination complexes discussed here. Molecular models indicate that there is considerable rotational freedom around the Ar–CH_2–N bonds, in particular around the CH_2–N bond, thus allowing the C–H(ortho) bond to evade a possibly destabilizing axial interaction. Such rotations are indeed observed in the bis-ortho-substituted complexes **8a** and **8b**, as discussed above. As, however, the low-field shift of the ortho proton in the NMR-spectrum of **7c** is present even at 100 °C (in DMSO-d_6) and does not vary with temperature, a stabilizing interaction that results from such an axial approach seems more likely for the monosubstituted complexes [PdX_2{R–CH–N–N}]. Similar C–H- -M interactions which give rise to low-field shifts have been proposed to be present in some platinum complexes, and weak coupling with the platinum center has been taken as evidence for some covalent character of a Pt- -H interaction.[29] However, the exact nature of this interaction is not clear. Since the $^1J_{CH(ortho)}$ value in the proton coupled ^{13}C spectrum of, for

(34) (a) Sudmeier, J. L.; Blackmer, G. L. *Inorg. Chem.* **1971**, *10*, 2010. (b) Hawkins, C. J.; Peachey, R. M. *Aust. J. Chem.* **1976**, *29*, 33.
(35) Nielson, A. J. *Transition Met. Chem.* **1981**, *6*, 180.
(36) The ^{1}H NMR spectrum obtained by adding 1 equiv of **1g** to $Pd(OAc)_2$ in CD_3OD corresponds primarily to **10a** (by comparison with data for **10b**) and <20% of species which may contain monocoordinated ligand. This in situ NMR spectrum of **10a** is very different to that of the redissolved solid material isolated by addition of 1 equiv of **1g** to $Pd(OAc)_2$ and washing with Et_2O. The NMR spectrum of the isolated material showed much too strong resonances of the acetate groups. This result indicates that **1g** only weakly coordinates to palladium acetate (probably because of the severe steric crowding around the two nitrogen donors) and that it is partly washed out during the work-up.
(37) (a) Deeming, A. J.; Rothwell, I. P. *Pure Appl. Chem.* **1980**, *52*, 649. (b) Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117.

example, **7c** is normal (163 Hz), a description as an agostic Pd- -H- -C interaction (which would moreover lead to a high-field shift of the proton)[38] can be excluded.

Our proposal is that for the cyclopalladation of aryl rings an oblique approach of the ortho proton and ortho carbon atom toward the palladium center is very favorable. That is not to say that such an approach is necessary, but that the activation energy of the ortho metalation may be substantially lower for ligands in which such an approach is possible than for ligands for which this is not the case. As already discussed above, the ortho C–H bond in **7e** is ideally positioned with respect to the square coordination plane around the palladium center for an electrophilic attack of Pd on the ortho carbon atom with concomitant elimination of HX. This provides an explanation for the preferential attack of the palladium center on the benzylic C–H bonds in **1g**. The coplanar position (with respect to the square planar coordination plane around Pd) of the N–CH_2Ph bond in the coordination adduct **10a** prevents an oblique approach as found for **7e**. This is substantiated by the ^{1}H NMR spectrum of **10a**, which indicates that there is no interaction between the ortho protons of the phenyl ring and the metal center in solution. Therefore, the activation energy for attack on the aromatic ring is relatively high and an alternative pathway, i.e., benzylic attack, prevails. The reason for the high selectivity for aromatic metalation over benzylic attack in ligand **1c** can be found clearly in the crystal structure of **7e**, where the ortho hydrogen atom is in close proximity to the metal and the 2-substituent is pointing away from palladium. Such as oblique approach provides a link between the 16-electron path and the 14-electron path for cyclometalation; the C–H activation takes place in a three coordinate, 14-electron species, but the necessary ligand dissociation is initiated by the oblique approach of the C–H bond toward the 16-electron complex.

Experimental Section

General. C_6H_6, Et_2O, and pentane were freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 or Bruker AC 300 spectrometers. Elemental analyses were carried out either by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands, or by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a. d., Ruhr, Germany.

Synthesis of *N*-Benzyl-*N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (1a). To a solution of *N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (12.4 g; 0.12 mol) in C_6H_6 (100 mL) was added dropwise (under a N_2 atmosphere) benzyl bromide (21 g; 0.12 mol) in the course of 2.5 h. After the addition, the resulting two-phase system was stirred for another hour. Next, the mixture was treated with a solution of NaOH (30 g; excess) in water (100 mL), Et_2O (100 mL) was added, and the organic layer, including a viscous syrup, was separated from the aqueous phase. The organic part was dried over NaOH pellets. The C_6H_6/Et_2O solution was decanted from the NaOH/syrup mass. The latter was extracted thoroughly with Et_2O (4 × 75 mL). The combined extracts and decanted solution were evaporated with a rotary evaporator, and the residue was distilled in vacuo to give the product as a colorless oil (9.0 g; 39%). Bp: 85 °C/0.1 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.27 (m, 5 H, Ar*H*); 3.52 (s, 2 H, ArCH_2N); 2.45 (m, 4 H, NCH_2CH_2N); 2.23 (s, 3 H, NCH_3); 2.20 (s, 6 H, N$(CH_3)_2$).

Synthesis of *N*-(2-Chlorobenzyl)-*N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (1b). From 2-chlorobenzyl chloride and *N*,*N*′,*N*′-trimethyl-1,2-diaminoethane in C_6H_6 at reflux. Colorless oil; yield 40%. Bp: 100–120 °C/0.5 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.46, 7.32 (dd, 1 H, Ar*H*(ortho)); 7.17 (m, 2 H, Ar*H*); 3.61 (s, 2 H, ArCH_2N); 2.55, 2.45 (m, 2 H, NCH_2); 2.25 (s, 3 H, NCH_3); 2.21 (s, 6 H, N$(CH_3)_2$).

Synthesis of *N*-(2-Methylbenzyl)-*N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (1c). From 2-methylbenzyl bromide and *N*,*N*′,*N*′-trimethyl-1,2-diaminoethane in C_6H_6. Slightly yellow oil; yield 35%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.25 (m, 1 H, Ar*H*); 7.13 (m, 3 H, Ar*H*); 3.46 (s, 2 H, ArCH_2N); 2.52, 2.44 (m, 2 H, NCH_2); 2.36 (s, 3 H, ArCH_3); 2.23 (s, 3 H, NCH_3); 2.20 (s, 6 H, N$(CH_3)_2$).

Synthesis of *N*-(2-Bromobenzyl)-*N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (1d). From 2-bromobenzyl bromide and *N*,*N*′,*N*′-trimethyl-1,2-diaminoethane in C_6H_6 in the presence of Et_3N (5 equiv). Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.49 ("t", 2 H, Ar*H*(ortho)); 7.25, 7.11 (t, 1 H, Ar*H*); 3.59 (s, 2 H, ArCH_2N); 2.55, 2.45 (m, 2 H, NCH_2); 2.26 (s, 3 H, NCH_3); 2.21 (s, 6 H, N$(CH_3)_2$).

Synthesis of *N*-(2,4,6-trimethylbenzyl)-*N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (1e). To a solution of *N*,*N*′,*N*′-trimethyl-1,2-diaminoethane (18.4 g; 0.18 mol) in toluene (250 mL) at reflux, containing finely powdered anhydrous Na_2CO_3 (100 g), was added dropwise with vigorous mechanical stirring a solution of 2,4,6-trimethylbenzyl chloride (27.0 g; 0.16 mol) in toluene (100 mL). After being stirred for 18 h at reflux temperature under a N_2 atmosphere, the mixture was cooled, and water was added to dissolve the Na_2CO_3. The organic phase was collected, and the aqueous layer was extracted with Et_2O (3 × 100 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was removed with a rotary evaporator. Vacuum distillation of the oily residue afforded the product (22.9 g; 61%) as a slightly yellow oil. Bp: 160–163 °C/2.5 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.35 (s, 2 H, Ar*H*); 3.48 (s, 2 H, ArCH_2N); 2.55, 2.45 (m, 2 H, NCH_2); 2.40 (s, 6 H, *o*-ArCH_3); 2.28 (s, 3 H, NCH_3); 2.23 (s, 6 H, N$(CH_3)_2$; 2.20 (s, 3 H, *p*-ArCH_3).

Synthesis of 6-[2-(*N*,*N*-dimethylamino)ethyl]-1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (1f). To a solution of NaI (75 g; 0.5 mol; dried for 16 h at 170 °C in vacuo) in a mixture of DME (DME = 1,2-dimethoxyethane) and 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (170 mL; 1 mol) was added dropwise (3 h) at reflux temperature a solution of *N*-(2-chloroethyl)dimethylamine hydrochloride (33 g; 0.23 mol) in absolute ethanol (500 mL) under a N_2 atmosphere. The mixture was heated under reflux for 30 h. Solvents were distilled off at normal pressure. The remaining brown viscous syrup was treated with an aqueous solution of NaOH (50 g/250 mL) and dried over NaOH pellets after removal of the aqueous layer. Distillation afforded the product (14.1 g; 27%) as a slightly yellow oil. Bp: 105 °C/0.1 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.01 (m, 1 H, NC*H*C$_2$); 2.88, 2.09 (dd, 1 H, NC*H*HC within azabicyclooctane unit); 2.71, 2.57 (m, 1 H, NC*H*HC within ethylenediamine unit); 2.29 (t, 2 H, Me_2NCH_2 within ethylenediamine unit); 2.20 (s, 6 H, N$(CH_3)_2$); 1.52 (m, 2 H, C$_2$C*H*H); 1.37 (dt, 1 H, C$_2$C*H*H); 1.25, 1.16 (dd, 1 H, C$_2$C*H*H); 1.18, 0.97, 0.84 (s, 3 H, CCH_3); 1.02 (d, 1 H, C$_2$C*H*H).

Synthesis of *N*-(2,4,6-Trimethylbenzyl)-*N*′-benzylpiperazine (1g). A solution of *N*-benzylpiperazine (26.11 g; 0.15 mol) and 2,4,6-trimethylbenzyl chloride (25 g; 0.15 mol) in a mixture of C_6H_6 (200 mL) was stirred for 24 h at room temperature under a N_2 atmosphere. A small amount of a white precipitate was formed during this time. The mixture was heated at reflux for an additional 24 h, which resulted in the formation of more precipitate. After cooling and dilution with Et_2O (200 mL), the mixture was treated with a solution of NaOH (55 g) in water (125 mL). The organic phase was separated from the aqueous layer and an insoluble heavy syrup by decantation, and the organic phase was dried over NaOH pellets. After filtration, rotary evaporation of the solvents gave 42 g of a thick syrup which, based on its ^{1}H NMR spectrum, contained about 80% product. Dissolution of the syrup in some hexane and subsequent cooling to −30 °C gave a white waxy precipitate which (after decanting the supernatant liquid) was washed with water (3 × 50 mL). The white waxy material was taken up in Et_2O, and the solution was

(38) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

dried over NaOH pellets. After removal of the Et_2O in vacuo the remaining material was boiled for 30 min in MeOH, containing Norit A (activated carbon; several grams) and alumina (neutral; several tens of grams). After filtration and evaporation of the MeOH, treatment of the oily residue with a small amount of cold (−30 °C) Et_2O afforded a white powder upon vigorous scratching. Yield: 21 g (45%). The product was ca. 95% pure according to its ^1H NMR spectrum. Since the impurity did not interfer with the cyclopalladation reaction, no attempts were made to further improve the purity of this compound. The compound solidifies with great difficulty and is normally obtained as a waxy solid. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.37 (m, 5 H, phenyl $C_6H_5CH_2$); 6.90 (s, 2 H, 2,4,6-$Me_3C_6H_2CH_2$); 3.56, 3.52 (s, 2 H, $ArCH_2N$); 2.52 (broad, 8 H, NCH_2 within piperazine unit); 2.43 (s, 6 H, o-$ArCH_3$); 2.34 (s, 3 H, p-$ArCH_3$).

Synthesis of *N*-(2-Phenylethyl)-*N*'-methylpiperazine (1h). To a solution of *N*-methylpiperazine (30 mL; 0.27 mol) in MeOH (100 mL), cooled in an ice/water bath, was added trifluoroacetic acid (21 mL; 0.27 mol) (1 equiv of acid was added to avoid quaternization of the methyl-substituted nitrogen).[39] A white precipitate formed. The mixture was brought to reflux, which resulted in complete dissolution of the precipitate. To the boiling solution was added dropwise (2-bromoethyl)benzene (37 mL; 0.27 mol). The mixture was refluxed for 3 days under a N_2 atmosphere. The solvents were removed by rotary evaporation, and the sticky residue was washed with Et_2O (1 × 300 mL; 3 × 150 mL). The yellow-white paste was treated with a solution of NaOH (50 g) in water (200 mL), and the organic products were extracted with Et_2O (250 mL). The aqueous layer was extracted once more with Et_2O (250 mL), and the combined organic layers (including an insoluble syrup) were dried over NaOH pellets. After filtration and removal of the solvents in vacuo, a yellow syrup remained. This was dissolved in Et_2O (150 mL), and the product was precipitated in the form of its diammonium salt by addition of 30% hydrochloric acid (32 mL) while the mixture was cooled with ice. The Et_2O/water mixture was decanted, and the white precipitate was washed again with Et_2O (3 × 100 mL). Deprotonation with aqueous NaOH (20 g/200 mL), extraction with Et_2O (300 mL), and drying on NaOH pellets afforded a yellow oil after rotary evaporation of the solvent. This was distilled in vacuo to give 17 g (30%) of a colorless oil. Bp: 115–120 °C/0.01 mmHg). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.23 (m, 2 H, Ar*H*); 7.16 (m, 3 H, Ar*H*); 2.77, 2.56 (m, 2 H, $ArCH_2CH_2N$); 2.45 (broad, 8 H, NCH_2 within piperazine unit); 2.25 (s, 3 H, NCH_3).

Synthesis of [PdCl{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (2a). A mixture of $Pd(OAc)_2$ (2.86 g; 12.74 mmol) and **1a** (2.45 g; 12.74 mmol) in MeOH (400 mL) was heated under reflux for 20 h. After being cooled to room temperature, the yellow solution was filtered (black Pd^0 precipitate), and addition of a solution of LiCl (2.00 g; 47 mmol) in MeOH (20 mL) resulted in the precipitation of a yellow–white solid. The precipitate was isolated by filtration and washed with MeOH (4 × 20 mL), Et_2O (4 × 20 mL), and pentane (4 × 20 mL) to afford **2a** (3.20 g; 75%) as a pale yellow powder. Dec: >215 °C. IR (KBr) ν/cm^{-1}: 330 (PdCl). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 150.41 (quaternary Ar; one signal); 135.88, 125.65, 124.22, 121.88 (Ar); 71.43 ($ArCH_2N$); 61.66, 60.70 (NCH_2CH_2N); 49.93, 47.56, 46.74 (NCH_3). Anal. Calcd for $C_{12}H_{19}ClN_2Pd$: C, 43.26; H, 5.76; N, 8.41. Found: C, 43.10; H, 5.68; N, 8.40.

Synthesis of [PdI{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (2c). Prepared according to the procedure given for **2a**. Slightly yellow powder; yield 71% from **1a** after precipitation with KI. Crystals suitable for a single-crystal X-ray diffraction study were grown by slow evaporation of a saturated CD_2Cl_2 solution. Mp: 207 °C dec. Anal. Calcd for $C_{12}H_{19}IN_2Pd$: C, 33.94; H, 4.52; N, 6.59. Found: C, 34.27; H, 4.56; N, 6.61.

Synthesis of [PdCl{$C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)$-2-Cl-3}] (2d). Prepared according to the procedure given for **2a**. White powder; yield 92% from **1b** after precipitation with LiCl. An analytically pure sample was obtained by recrystallization from CH_2Cl_2, affording the product as slightly yellow crystals (0.27 g; 75%). Dec: >230 °C. IR (KBr) ν/cm^{-1}: 330 (PdCl). Anal. Calcd for $C_{12}H_{18}Cl_2N_2Pd$: C, 39.20; H, 4.95; N, 7.62. Found: C, 39.10; H, 5.01; N, 7.59.

Synthesis of [PdCl{$C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)$-2-Me-3}] (2e). Prepared according to the procedure given for **2a**. White powder; yield 71% from **1d** after precipitation with LiCl. Dec: >180 °C. IR (KBr) ν/cm^{-1}: 330 (PdCl). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 148.35, 146.44, 131.52 (quaternary Ar); 133.66, 125.92 (two coincident signals) (Ar); 69.22 ($ArCH_2N$); 61.52, 60.93 (NCH_2CH_2N); 49.90, 47.96, 46.70 (NCH_3); 20.71 ($ArCH_3$). Anal. Calcd for $C_{13}H_{21}ClN_2Pd$: C, 44.97; H, 6.11; N, 8.07. Found: C, 44.52; H, 6.15; N, 8.10.

Synthesis of [PdCl{$C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)$-2-MeO-3}] (2f). A mixture of **6f** (0.59 g; 1.48 mmol) and $AgNO_3$ (0.51 g; 3.00 mmol) in MeOH (125 mL) was stirred for 1.5 h in the dark. To the orange solution was added NaOAc (0.30 g; 3.66 mmol). AgCl was filtered off, and the clear yellow filtrate was heated under reflux for 6 h. The mixture was filtered, and the yellow filtrate was evaporated in vacuo until about 15 mL of solvent remained. To the solution was added LiCl (1.00 g; 24 mmol) dissolved in MeOH (10 mL). Further evaporation of the solution to a small volume and cooling caused the precipitation of a slightly yellow powder. This was washed with water (4 × 5 mL), MeOH (4 × 5 mL), and Et_2O (6 × 10 mL). Yield: 0.27 g of an off-white powder (50%). Dec: >210 °C. IR (KBr) ν/cm^{-1}: 1260 (ArOMe); 330 (PdCl). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 153.47, 147.63, 137.23 (quaternary Ar); 128.39, 126.22, 106.37 (Ar); 67.35 ($ArCH_2N$); 61.75, 60.84 (NCH_2CH_2N); 55.01 (OCH_3); 49.91, 47.09, 46.76 (NCH_3). Anal. Calcd for $C_{13}H_{21}ClN_2OPd$: C, 42.99; H, 5.84; N, 7.71. Found: C, 42.45; H, 5.69; N, 7.27.

Synthesis of [PdCl{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (3a). A mixture of $Pd(OAc)_2$ (1.12 g; 4.99 mmol) and **1e** (1.17 g; 4.99 mmol) in MeOH (40 mL) was heated on a water bath (60 °C) for 7 h. Metallic palladium was filtered off, and addition of a solution of LiCl (0.42 g; 10 mmol) in a small amount of MeOH to the filtrate afforded a yellow precipitate which was formed within 1 min. This was collected and washed with MeOH (4 × 2 mL) and Et_2O (4 × 3 mL). The product (1.57 g; 84%) was air dried. Dec: >180 °C. IR (KBr) ν/cm^{-1}: 300 (PdCl). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 146.24, 138.12, 135.54, 130.35 (quaternary Ar); 125.80, 125.66 (Ar); 59.12, 58.71, 58.10 ($ArCH_2N$, NCH_2CH_2N); 49.73, 47.72, 46.09 (NCH_3); 21.00, 19.91 ($ArCH_3$); 18.88 ($ArCH_2Pd$). Anal. Calcd for $C_{15}H_{25}ClN_2Pd$: C, 48.01; H, 6.73; N, 7.47. Found: C, 47.53; H, 6.81; N, 7.54.

Synthesis of [PdBr{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (3b). Prepared according to the procedure given for **3a**. Yellow powder after precipitation with LiBr; yield 87%. Dec: >190 °C. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 146.12, 138.44, 135.42, 130.64 (quaternary Ar); 125.91, 125.81 (Ar); 58.53, 58.34, 58.11 ($ArCH_2N$, NCH_2CH_2N); 50.20, 48.42, 46.65 (NCH_3); 21.03, 19.82 ($ArCH_3$); 17.63 ($ArCH_2Pd$). Anal. Calcd for $C_{15}H_{25}BrN_2Pd$: C, 42.92; H, 6.02; N, 6.68. Found: C, 42.63; H, 5.75; N, 6.60.

Synthesis of [PdI{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (3c). Prepared according to the procedure given for **3a**. Yellow-brown crystals after precipitation with LiI; yield 74%. Suitable crystals for an X-ray diffraction study were obtained by diffusion of Et_2O into a solution of the compound in CH_2Cl_2. Dec: >200 °C. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 145.55, 138.59, 135.28, 131.08 (quaternary Ar); 126.25, 125.74 (Ar); 58.02, 57.59 (two coincident signals) ($ArCH_2N$, NCH_2CH_2N); 51.22, 49.60, 47.19 (NCH_3); 21.06, 19.68 ($ArCH_3$); 14.77 ($ArCH_2Pd$). Anal. Calcd for $C_{15}H_{25}IN_2Pd$: C, 38.60; H, 5.41; N, 6.00. Found: C, 38.30; H, 5.27; N, 6.07.

Synthesis of [PdMe{$CH_2C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-2-$Me_2$-3,5}] (3e). To a suspension of **2a** (1.50 g; 4.00 mmol) in anhydrous Et_2O (250 mL) was added 2.50 mL of a 1.60 M solution of MeLi in Et_2O at −30 °C under a N_2 atmosphere. The mixture was allowed to warm to room temperature in the course of 2.5

(39) (a) Moore, T. S.; Boyle, M.; Thorn, V. M. *J. Chem. Soc.* **1929**, 39. (b) Baltzly, R.; Buck, J. S.; Lorz, E.; Schön, W. *J. Am. Chem. Soc.* **1944**, *66*, 263.

Table VI. Crystal Data and Details of the Structure Determination

	2c	3c	7e
		Crystal Data	
emp formula	$C_{12}H_{19}IN_2Pd$	$C_{15}H_{25}IN_2Pd$	$C_{12}H_{19}I_3N_2Pd$
form wt	424.62	466.70	678.43
cryst syst	orthorhombic	monoclinic	triclinic
space grp	*Pnaa* (nonstandard setting of No. 56)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.5216(3)	9.506(1)	8.545(1)
b (Å)	17.6034(5)	13.582(1)	8.797(1)
c (Å)	18.8696(8)	13.148(1)	13.829(1)
α (deg)			81.77(1)
β (deg)		91.36(4)	75.47(1)
γ (deg)			63.33(1)
V (Å^3)	2830.61(18)	1697.2(3)	898.7(2)
Z	8	4	2
D_{calc} (g cm^{-3})	1.993	1.826	2.507
F(000) (electrons)	1632	912	620
μ(Mo Kα) (cm^{-1})	34.3	28.7	61.1
cryst size (mm)	0.25 × 0.25 × 0.05	0.05 × 0.57 × 0.57	0.03 × 0.30 × 0.50
		Data Collection	
temp (K)	295	295	295
radn (Mo Kα; Zr-filtered) (Å)	0.71073	0.71073	0.71073
θ_{min}, θ_{max} (deg)	1.08, 30.0	1.5, 27.5	1.52, 28.47
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$ (deg)	0.60 + 0.35 tan θ	0.60 + 0.35 tan θ	1.30 + 0.35 tan θ
hor. and ver. aperture (mm)	3.00, 6.00	3.00, 5.00	4.00, 6.00
ref refln(s)	−4 3 3; −4 −3 −3	3 0 2; 2 −3 0; 0 2 3	1 0 4; 1 −2 0; 0 2 −1
data set	h −11 to 0; k 0–24; l 0–26	h −12 to +12; k 0–17; l −17 to 0	h −9 to +11; k 0–11; l −18 to +18
total; unique data	4623; 4110	7718; 3893	4389; 4371
obsd data ($I > 2.5\sigma(I)$)	2678	3326	2810
		Refinement	
no. of refined param	157	249	175
R, R_w, S	0.038, 0.035, 2.77	0.021, 0.026, 0.79	0.064, 0.071, 2.35
weighting scheme (w^{-1})	$\sigma^2(F)$	$\sigma^2(F) + 0.0001F^2$	$\sigma^2(F)$
$(\Delta/\sigma)_{av}$	0.003	0.02	0.002
max. resid density (e/Å^3)	0.70	0.73	2.20 (near I)

h. To the yellow solution (with a small amount of an insoluble brown material) was added water (6 mL), after which the mixture was cooled to −30 °C. The Et_2O was decanted from the frozen water and the cold solution filtered through $MgSO_4$. After evaporation of the solvent in vacuo, the remaining yellow solid was washed quickly with cold (−30 °C) pentane (4 × 10 mL). The slightly yellow powder was dried in vacuo and stored under a N_2 atmosphere. Yield 1.25 g (88%). The methylation is much less clean when **2b** instead of **2a** is used as starting material. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δ: 152.46, 137.33, 134.78, 129.02 (quaternary Ar); 126.40, 124.07 (Ar); 59.75, 57.63, 55.94 (ArCH_2N, NCH_2CH_2N); 49.91, 48.34, 42.95 (NCH_3); 21.37, 20.51 (ArCH_3); 19.36 (ArCH_2Pd); −7.22 (PdCH_3). Anal. Calcd for $C_{16}H_{28}N_2Pd$: C, 54.15; H, 7.97; N, 7.90. Found: C, 53.66; H, 7.73; N, 7.80.

Synthesis of [PdCl{$CH_2C(Me)CH_2CHN(CH_2CH_2NMe_2)$-$CH_2C(Me)(CH_2)CH_2$}] (4a). A solution of $Pd(OAc)_2$ (1.12 g; 4.99 mmol) and **1f** (1.13 g; 5.04 mmol) in MeOH (250 mL) was heated at 60 °C for 14 h. Metallic palladium was filtered off over Celite, and LiCl (1.12 g; excess) was added to the clear yellow filtrate. Rotary evaporation afforded a slightly yellow powder. The product was taken up in CH_2Cl_2 (150 mL), after which the solution was filtered and concentrated to a small volume (5 mL). Addition of Et_2O (50 mL) afforded a slightly yellow powder, which was isolated by filtration and washed with Et_2O (5 × 20 mL) and pentane (30 mL). Yield: 1.68 g (92%). Dec: >160 °C. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 74.26, 63.19, 59.28 (NCH_2C); 66.93 (NCHC_2); 51.50, 51.44, 41.72 (CCH_2C); 48.37, 46.54 (NCH_3); 41.40, 33.36 (quaternary C); 32.78, 24.12 (CCH_3), 31.98 (CH_2Pd). Anal. Calcd for $C_{14}H_{27}ClN_2Pd$: C, 46.03; H, 7.47; N, 7.67. Found: C, 45.70; H, 7.59; N, 7.75.

Synthesis of [PdCl{$CH_2C_6H_2(CH_2N(CH_2CH_2)_2NCH_2Ph$)-2-$Me_2$-3,5}] (5a). A mixture of $Pd(OAc)_2$ (0.53 g; 2.36 mmol) and **1g** (0.80 g; 2.59 mmol) in MeOH (100 mL) was stirred for 20 h at 60 °C. After filtration over Celite, LiCl (1 g; excess) in MeOH (10 mL) was added to the brown solution. The mixture was concentrated to 20 mL, which resulted in precipitation of a yellow solid. After further cooling to −30 °C, this solid was collected and washed with MeOH (4 × 7.5 mL), Et_2O (3 × 20 mL), and pentane (1 × 20 mL). Yield: 0.56 g (50%). An analytically pure crystalline sample was obtained by diffusion of Et_2O into a CH_2Cl_2 solution of **5a**. Dec: >190 °C. IR (KBr) ν/cm^{-1}: 310 (PdCl). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 146.79, 138.63, 136.21, 132.29, 129.92 (quaternary Ar); 130.96, 128.49, 128.39, 126.53, 125.82 (Ar); 61.63, 55 (very broad), 54.17, 50.5 (broad) (CH_2N); 20.92, 20.01 (two coincident signals) (ArCH_3, ArCH_2Pd). Anal. Calcd for $C_{21}H_{27}ClN_2Pd$: C, 56.13; H, 6.06; N, 6.23. Found: C, 56.05; H, 6.09; N, 6.21.

Synthesis of [PdOAc{$C_6H_4(CH_2CH_2N(CH_2CH_2)_2NMe$)-2}] (5c). $Pd(OAc)_2$ (0.126 g; 0.56 mmol) and **1h** (0.114 g; 0.56 mmol) were dissolved in CD_3OD (1.2 mL) in an NMR tube. The tube was heated for 20 h at 60 °C. The ^1H NMR spectrum of the brown solution showed the formation of **5c** in about 65% yield. The solution was filtered and cooled to −30 °C. The resulting grayish crystals were isolated by filtration and washed with Et_2O (4 × 3 mL). The product was redissolved in CH_2Cl_2, and the solution was filtered again over Celite to remove traces of metallic palladium. Evaporation of the solvent to small volume (3 mL) afforded some white powder, and further precipitate was formed by addition of a 10-fold excess of Et_2O. The supernatant was decanted from the product, which was washed with pentane (20 mL) and dried in vacuo. Yield: 0.12 g of an off-white powder (58%). IR (KBr) ν/cm^{-1}: 1610, 1370 (OAc). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 177.84 (OC(O)Me); 139.81, 139.04 (quaternary Ar); 134.36, 126.19, 124.49, 123.99, 123.88 (Ar); 57.69, 57 (very broad), 54.23 (CH_2N); 44.75 (NCH_3); 37.34 (ArCH_2); 24.02 (OC(O)CH_3).

Synthesis of [PdCl{$C_6H_4(CH_2CH_2N(CH_2CH_2)_2NMe$)-2}] (5d). This product was prepared in quantitative yield by addition of a 10-fold excess of LiCl (dissolved in MeOH) to a warm (40 °C) solution of **5c** in MeOH. After being cooled to room temperature, the microcrystalline white material was isolated by filtration and washed with MeOH (5 × 2 mL), Et_2O (5 × 2 mL),

and pentane (5 × 2 mL). Dec: > 180 °C. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 139.82, 139.55 (quaternary Ar); 139.04, 126.71, 124.75, 124.20, 124.09 (Ar); 57.63, 54.43 (CH_2N); 45.81 (NCH_3); 38.01 ($ArCH_2$) (**5d** has poor solubility and one CH_2N group is not visible; it is probably broad (cf. ^{13}C data for **5c**). Anal. Calcd for $C_{13}H_{19}ClN_2Pd$: C, 45.23; H, 5.56; N, 8.12. Found: C, 45.10; H, 5.42; N, 8.10.

Synthesis of [PdBr{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (2b). To a solution of $Pd(dba)_2$ (1.14 g; 1.98 mmol) in C_6H_6 (125 mL) was added **1c** (0.57 g; 2.10 mmol) in C_6H_6 (4 mL) under a N_2 atmosphere. The mixture was slowly heated on a waterbath, and at a bath temperature of 80 °C the purple solution slowly turned brownish-yellow with simultaneous precipitation of an off-white solid. After 15 min at 80 °C the bath was removed and the mixture was allowed to cool to room temperature. The precipitate was filtered off and washed with Et_2O (5 × 20 mL). The gray solid was taken up in CH_2Cl_2 (300 mL), and the solution was filtered (metallic palladium residue) to give a clear yellow filtrate. The solvent was removed in vacuo, and the solid residue was washed with Et_2O (3 × 20 mL). After being dried in vacuo, the product was obtained as a greenish-white solid (0.72 g; 96%). Dec: >200 °C. Anal. Calcd for $C_{12}H_{19}BrN_2Pd$: C, 38.16; H, 5.08; N, 7.42. Found: C, 37.60; H, 4.83; N, 7.07.

Starting from **1b**, complex **2a** can be obtained in 69% yield using a similar procedure as described above except that the mixture was stirred for 12 h at 80 °C.

Synthesis of [Pd(ONO_2){$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (2g). A mixture of **2a** (1.27 g; 3.81 mmol) and $AgNO_3$ (0.65 g; 3.82 mmol) in MeOH (200 mL) was stirred for 15 h in the absence of light. The silver chloride precipitate formed was filtered off. The solvent was removed in vacuo, and the residue was taken up in CH_2Cl_2. The solution was filtered again. Evaporation of the filtrate to dryness afforded the product as a slightly yellow powder, which was washed with Et_2O. Yield: 1.36 g (99%). Mp: 195 °C dec. IR (KBr) ν/cm^{-1}: 1460, 1380, 1270 (ONO_2). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 149.71, 145.58 (quaternary Ar); 132.36, 125.35, 124.85, 121.89 (Ar); 71.76 ($ArCH_2N$), 61.01 (NCH_2CH_2N); 50.24, 48.38, 46.76 (NCH_3). Anal. Calcd for $C_{12}H_{19}N_3OPd$: C, 40.06; H, 5.33; N, 11.68. Found: C, 39.82; H, 5.32; N, 11.63.

Synthesis of [Pd(NO_2){$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}] (2h). To a suspension of **2b** (0.50 g; 1.18 mmol) in acetone (30 mL) was added $AgNO_2$ (0.20 g; 1.30 mmol). The mixture was stirred for 2.5 h. After evaporation of the solvent, the gray solid was taken up in CH_2Cl_2 (35 mL). The suspension was filtered, and the filtrate was evaporated to dryness. The product was obtained as a white powder (0.40 g; 99%). Dec: >225 °C. IR (KBr) ν/cm^{-1}: 1365, 1310 (NO_2).

Synthesis of [Pd{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2}(2,6-lutidine)]Otf (2k). To a solution of **2a** (0.217 g; 0.650 mmol) in CH_2Cl_2 (50 mL) was added a solution of AgOtf (0.168 g; 0.652 mmol) in CH_2Cl_2 (6 mL) containing 10 drops of acetonitrile. Silver chloride was filtered off, and 2,6-lutidine (0.087 g; 0.812 mmol) in CH_2Cl_2 (2 mL) was added to the colorless filtrate. Evaporation of the solvent in vacuo afforded a colorless syrup. This was treated with cold Et_2O to give a white powder. After being washed with Et_2O (4 × 4 mL), the white solid was dried in vacuo (0.34 g; 94%). Dec: >200 °C. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 159.57, 158.78, 151.11, 145.21 (quaternary Ar); 139.28, 131.89, 125.81, 125.23, 123.84, 123.74, 123.10 (Ar); 120.93 (Otf, q, $^1J_{CF}$ = 321 Hz); 71.09 ($ArCH_2N$), 62.09, 60.49 (NCH_2CH_2N); 50.95, 48.66, 47.53 (NCH_3); 28.29, 27.96 (lutidine CH_3). Anal. Calcd for $C_{20}H_{28}F_3N_3O_3SPd$: C, 43.36; H, 5.10; N, 7.59. Found: C, 43.27; H, 5.21; N, 7.69.

Synthesis of [Pd(ONO_2){$CH_2C(Me)CH_2CHN(CH_2CH_2NMe_2)CH_2C(Me)(CH_2)CH_2$}] (4b). Preparation as for **2g**. Slightly yellow powder. Yield: 96%. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 75.19, 63.91, 59.10 (NCH_2C); 67.37 ($NCHC_2$); 51.86, 51.57, 41.73 (CCH_2C); 48.16, 46.85 (NCH_3); 41.58, 33.92 (quaternary C); 32.04, 24.15 (CCH_3), 34.81 (CH_2Pd). Anal. Calcd for $C_{14}H_{27}N_3O_3Pd$: C, 42.91; H, 6.96; N, 10.73. Found: C, 42.66; H, 6.97; N, 10.68.

Table VII. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 2c ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$)

atom	x	y	z	U(eq), Å^2
I	0.385 48(4)	0.090 02(2)	0.099 23(2)	0.0416(1)
Pd	0.112 33(4)	0.117 11(2)	0.044 27(2)	0.0250(1)
N(1)	–0.1000(5)	0.1490(2)	0.0007(2)	0.0307(12)
N(2)	–0.0185(5)	0.1146(3)	0.1443(2)	0.0337(16)
C(1)	0.1870(6)	0.1292(3)	–0.0555(3)	0.0287(17)
C(2)	0.3151(7)	0.0985(3)	–0.0892(3)	0.0373(17)
C(3)	0.3386(7)	0.1120(4)	–0.1613(3)	0.053(2)
C(4)	0.2364(8)	0.1553(4)	–0.1992(3)	0.060(3)
C(5)	0.1071(7)	0.1865(4)	–0.1669(3)	0.051(2)
C(6)	0.0806(6)	0.1737(3)	–0.0947(3)	0.0390(17)
C(7)	–0.0572(6)	0.2056(3)	–0.0559(3)	0.0360(17)
C(8)	–0.1918(6)	0.1819(3)	0.0601(3)	0.042(2)
C(9)	–0.1863(7)	0.1283(3)	0.1222(3)	0.0437(19)
C(10)	–0.1882(7)	0.0852(3)	–0.0335(3)	0.042(2)
C(11)	0.0358(8)	0.1786(4)	0.1895(3)	0.056(3)
C(12)	–0.0093(8)	0.0434(3)	0.1851(3)	0.051(2)

Table VIII. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 3c ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$)

atom	x	y	z	U(eq), Å^2
I	0.095 75(2)	0.011 21(1)	0.237 59(1)	0.0477(1)
Pd	0.108 23(2)	0.139 68(1)	0.383 69(1)	0.0338(1)
N(1)	0.1221(2)	0.241 76(15)	0.504 99(15)	0.0395(6)
N(2)	–0.1199(2)	0.172 59(16)	0.388 42(17)	0.0431(6)
C(1)	0.3597(2)	0.238 40(18)	0.353 59(18)	0.0383(7)
C(2)	0.4336(3)	0.2537(2)	0.2646(2)	0.0439(8)
C(3)	0.4710(3)	0.3474(2)	0.2325(2)	0.0491(9)
C(4)	0.4292(3)	0.4272(2)	0.2898(2)	0.0527(9)
C(5)	0.3542(3)	0.416 43(19)	0.3789(2)	0.0460(8)
C(6)	0.3211(3)	0.321 15(18)	0.411 39(19)	0.0401(7)
C(7)	0.3215(3)	0.138 01(19)	0.3861(2)	0.0438(8)
C(8)	0.5565(4)	0.3620(3)	0.1389(3)	0.0650(13)
C(9)	0.3130(5)	0.5073(2)	0.4373(4)	0.0683(13)
C(10)	0.2534(3)	0.3017(2)	0.5115(2)	0.0448(8)
C(11)	0.1076(4)	0.1915(2)	0.6046(2)	0.0569(10)
C(12)	–0.0010(3)	0.3073(2)	0.4826(2)	0.0498(9)
C(13)	–0.1336(3)	0.2478(3)	0.4694(3)	0.0570(10)
C(14)	–0.2103(4)	0.0867(3)	0.4107(3)	0.0642(11)
C(15)	–0.1654(4)	0.2146(3)	0.2896(3)	0.0599(11)

Synthesis of [$PdCl_2${$C_6H_5(CH_2N(Me)CH_2CH_2NMe_2)$}] (7a). To a solution of **1a** (0.23 g; 1.20 mmol) in MeOH (2.5 mL) was added 5.0 mL of a 0.23 M solution of Li_2PdCl_4 in MeOH (1.15 mmol Li_2PdCl_4). Within 3 min a yellow-orange precipitate was formed. This was filtered off and washed with MeOH (4 × 2.5 mL) and Et_2O (4 × 5 mL). Yield: 0.40 g (94%) of an orange powder. This complex does not cyclopalladate when heated under reflux in MeOH for 22 h. Dec: >215 °C. IR (KBr) ν/cm^{-1}: 320 (PdCl). Anal. Calcd for $C_{12}H_{20}Cl_2N_2Pd$: C, 38.99; H, 5.46; N, 7.58. Found: C, 38.93; H, 5.36; N, 7.44.

Synthesis of [$PdCl_2${$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-Cl-2}] (7b). Prepared according to the procedure given for **7a**. Yield: 96%. Dec: >200 °C. IR (KBr) ν/cm^{-1}: 320 (PdCl). Anal. Calcd for $C_{12}H_{19}Cl_3N_2Pd$: C, 35.67; H, 4.75; N, 6.93. Found: C, 35.53; H, 4.77; N, 6.90.

Synthesis of [$PdCl_2${$C_6H_2(CH_2N(Me)CH_2CH_2NMe_2)$-$Me_3$-2,4,6}] (8a). Prepared according to the procedure given for **7a**. Yield 80%. No cyclopalladation occurred when this compound was heated under reflux in 1,2-dichloroethane; after 4 days only starting material was recovered. Dec. >210 °C. IR (KBr) ν/cm^{-1}: 320 (PdCl). Anal. Calcd for $C_{15}H_{26}Cl_2N_2Pd$: C, 43.75; H, 6.38; N, 6.81. Found: C, 43.31; H, 6.42; N, 6.91.

Synthesis of [Pd($OAc)_2${$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-Cl-2}] (7c). To a solution of $Pd(OAc)_2$ (0.1089 g; 0.4851 mmol) in (20 mL) was added **1b** (0.1100 g; 0.4851 mmol), dissolved in C_6H_6 (4 mL). Removal of the solvent in vacuo afforded a yellow powder. This was treated with Et_2O to effect complete solidification. The yellow product was isolated by filtration and dried

Table IX. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 7e ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$)

atom	x	y	z	U(eq), Å²
I(1)	0.095 35(14)	0.227 61(12)	0.671 34(9)	0.0795(4)
I(2)	−0.352 62(14)	0.324 53(11)	0.647 96(7)	0.0615(3)
I(3)	−0.1394(2)	0.953 39(17)	0.931 67(16)	0.1372(8)
Pd	−0.196 84(11)	0.504 30(10)	0.673 11(7)	0.0369(3)
N(1)	−0.4237(12)	0.7358(10)	0.6634(7)	0.039(3)
N(2)	−0.0833(12)	0.6603(12)	0.7027(8)	0.048(3)
C(1)	−0.1271(16)	0.6151(17)	0.8892(10)	0.052(4)
C(2)	−0.1686(17)	0.4776(18)	0.9167(11)	0.058(5)
C(3)	−0.285(2)	0.471(2)	1.0028(12)	0.079(6)
C(4)	−0.360(2)	0.598(3)	1.0669(14)	0.092(8)
C(5)	−0.320(2)	0.735(3)	1.0467(14)	0.095(7)
C(6)	−0.201(2)	0.745(2)	0.9567(14)	0.082(6)
C(7)	−0.0009(16)	0.6137(16)	0.7911(9)	0.052(4)
C(8)	−0.2322(18)	0.8354(14)	0.7122(12)	0.062(5)
C(9)	−0.3572(17)	0.8679(14)	0.6446(12)	0.059(5)
C(10)	0.0604(19)	0.658(2)	0.6137(12)	0.076(6)
C(11)	−0.5598(17)	0.7627(17)	0.7563(10)	0.060(4)
C(12)	−0.5078(19)	0.7543(17)	0.5776(11)	0.063(5)

in vacuo (0.2175 g; 99%). Dec: >150 °C. IR (KBr) ν/cm⁻¹: 1580, 1400 (OAc). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ: 178.12, 177.89 (MeC(O)O); 136.64 (proton coupled spectrum: d, $^1J_{C,H}$ = 163 Hz, *o*-H); 135.50, 130.31 (quaternary Ar); 130.95, 129.27, 128.81 (Ar); 62.52, 60.71, 55.79 (NCH_2); 51.24, 50.48, 49.03 (NCH_3); 23.71, 23.23 ($CH_3C(O)O$). Anal. Calcd for $C_{16}H_{25}ClN_2O_4Pd$: C, 42.58; H, 5.60; N, 6.21. Found: C, 41.83; H, 5.78; N, 6.19.

Synthesis of Pd(OAc)$_2${C$_6$H$_4$(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)-Me-2}] (7d). Prepared according to the procedure given for **7c**. Dec: >110 °C. IR (KBr) ν/cm⁻¹; 1580, 1410 (OAc).

Synthesis of [Pd(OAc)$_2${C$_6$H$_2$(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)-Me$_3$-2,4,6}] (8b). Prepared according to the procedure given for **7c**. Dec: >120 °C. IR (KBr) ν/cm⁻¹; 1570, 1400 (OAc).

Compounds **9**, **10a**, and **10b** were prepared in situ by mixing accurately weighed amounts (1:1 molar ratio) of $Pd(OAc)_2$ and organic compound (**1f**, **1g** and **1h**, respectively) in CD_3OD solution (see preparation of **5c**).

Synthesis of [PdI$_2${C$_6$H$_4$(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)-I-2}] (7e). To a solution of **2c** (0.16 g; 0.38 mmol) in CH_2Cl_2 (25 mL) was added a solution of I_2 (0.11 g; 0.43 mmol) in CH_2Cl_2 (5 mL). After being stirred for 2 min, the deep-red mixture was treated with an aqueous solution of $Na_2S_2O_3{\cdot}5H_2O$ (0.10 g; 0.40 mmol). The organic layer was separated from the aqueous phase, dried ($MgSO_4$), and evaporated in vacuo to give the product as a deep-red solid (0.25 g; 97%). Crystals suitable for X-ray diffraction were obtained by evaporation of a pentane-layered solution of the compound in CH_2Cl_2. Dec: >160 °C. Anal. Calcd for $C_{12}H_{19}I_3N_2Pd$: C, 21.24; H, 2.83; N, 4.13. Found: C, 21.40; H, 2.85; N, 4.23.

Synthesis of [PdCl$_2${C$_6$H$_4$(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)-Cl-2}] (7b). Through a suspension of **2a** (0.19 g; 0.57 mmol) in 1,2-dichloroethane (50 mL) was bubbled Cl_2 for 10 min. The suspension was heated under reflux for 1.5 h. After removal of the solvent, the solid residue was washed with pentane (20 mL). The solid was suspended in Et_2O to ensure complete solidification and the solvent evaporated in vacuo to give the product as an orange powder (0.22 g; 96%) whose physical and chemical properties were completely identical to those of the complex obtained from **1b** and Li_2PdCl_4.

Identification of [PdCl$_3${C$_6$H$_4$(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)-2}] (6) by ^{1}H NMR. A slow stream of Cl_2 was passed through a saturated solution of **2a** in $CDCl_3$ for 30 s. An orange, slightly turbid solution formed instantaneously. A NMR spectrum was recorded immediately (within 10 min).

Reaction of 3e with Methyl Iodide. An NMR tube containing a solution of **3e** (0.0120 g; 0.034 mmol) in acetone-d_6 (0.5 mL) was cooled to −78 °C, and MeI (10.0 μL; 0.161 mmol) was added with a microsyringe. The ^{1}H NMR spectrum recorded at −30 °C showed complete disappearance of **3e** and new singlets at 1.49 and 1.06 ppm (assigned to Pd(IV)CH_3 groups), and also two singlets for the aromatic protons at 6.88 and 6.90 ppm. Warming to room temperature resulted in the near-quantitative formation of **3c** (^{1}H NMR spectrum identical to that of the product obtained by cyclopalladation) and concomitant formation of ethane (singlet at 0.84 ppm[21c]).

Reaction of 3e with Acetyl Chloride. To a solution of **3e** (0.0210 g; 0.059 mmol) in anhydrous C_6D_6 (0.5 mL) was added acetyl chloride (4.3 μL; 0.060 mmol) under a N_2 atmosphere, and a yellow solid precipitated immediately. The precipitate was isolated by filtration, washed with pentane, and dried. The material (0.0200 g; 90%) was identified as pure **3a** from its ^{1}H NMR spectrum. The C_6D_6 filtrate was analyzed by ^{1}H NMR spectroscopy, and the only product was identified as acetone by addition of an authentic sample.

X-ray Data Collection, Structure Determination, and Refinement of 2c, 3c, and 7e. Crystal data and numerical details of the structure determinations are given in Table VI. Crystals were glued on top of a glass fiber. X-ray data were collected on an Enraf Nonius CAD4 diffractometer. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections and checked for the presence of higher lattice symmetry.[40] Intensity data were corrected for Lp and absorption (**2c** and **7e** with DIFABS,[41] **3c** with ABSORB[42]) and merged into unique sets. The structures were solved with the PATT option of SHELXS86[43] and subsequent difference Fourier techniques. Subsequent refinement was done on *F* by full-matrix least-squares treatment with SHELX76.[44] Hydrogen atoms were taken into account either at calculated positions (**2c**, **7e**) or located from a difference map and their positions refined (**3c**). All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles. Neutral scattering factors were taken from Cromer and Mann[45] and corrected for anomalous dispersion.[46] Geometrical calculations, including the thermal motion ellipsoid plots, were done with PLATON[47] on a DEC5000/ULTRIX system. All other calculations were done on a MicroVax-II cluster. Final coordinates and equivalent isotropic thermal parameters for **2c**, **3c**, and **7e** are given in Tables VII, VIII and IX, respectively.

Acknowledgment. We thank the Innovation Oriented Research Program on Catalysis for financial support (to P.L.A.). The Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for Scientific Research (NWO) are thanked for financial support (to A.L.S.). X-ray data were kindly collected by A. J. M. Duisenberg.

Supplementary Material Available: Conformational analysis of the NCH_2CH_2N–skeleton in the cyclometalated complexes and coordination adducts and tables of fractional coordinates of the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles of **2c**, **3c**, and **7e** (13 pages). Ordering information is given on any current masthead page. References 48 and 49 below are cited in the supplementary material.

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